

APPLIED WATER TECHNOLOGY

By

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1

FUNDAMENTALS OF CHEMISTRY

In order to deal intelligently with water systems and their problems one must be aware of the basic chemistry applying to water. This chapter summarizes pertinent fundamentals.

ELEMENTS AND COMPOUNDS

Matter is made up of elements and compounds. *Elements* are substances that can not be chemically decomposed to give two or more simpler substances. The names of elements are usually abbreviated in order to simplify chemical notations. For example:

TABLE 1.1
Examples of Chemical Symbols

Element	Chemical Symbol
Hydrogen	H
Calcium	Ca
Oxygen	O

A partial list of the 103 elements which have been discovered thus far is given in Appendix 1. This table contains certain other information in addition to the standard chemical symbols.^(1.1)

A *compound* is a substance composed of two or more elements chemically combined in definite proportions by weight. The individual elements have lost their identity and no longer are recognizable unless you chemically separate the compound into its constituent elements.

For example, water (H₂O) is composed of hydrogen and oxygen, but you recognize water as a unique substance with its own peculiar properties. We seldom stop to consider that water is made up of hydrogen and oxygen. If you hold up a glass of water you certainly do not see hydrogen and oxygen. You see a clear liquid compound which we call water.

MIXTURES

A *mixture* is made up of two or more substances which retain their own properties. Thus, if you mix salt and pepper you can (with some effort) physically separate the two materials because you can readily identify them as individual species. Salt and pepper are both compounds. Salt (NaCl) is composed of sodium (Na) and chlorine (Cl), which are both elements.

ATOMS AND ATOMIC WEIGHTS

The fact that elements combine in fixed ratios by weight suggests that elements are made up of particles or pieces of matter. These units of matter, which are called *atoms*, may be defined as the smallest particle of an element which can enter into chemical change.

Atoms are composed of *electrons*, *protons* and *neutrons*. The electrons and protons are charged particles and the mass of the atom is due almost entirely to the protons and neutrons in the nucleus. Electrons have negligible mass and are usually disregarded when calculating the mass of an atom. Their properties are summarized in Table 1.2.

TABLE 1.2
Properties of Subatomic Particles

Particle	Mass (Atomic Mass Units)	Electrical Charge
Electron	0.00055	-1
Proton	1.0	+1
Neutron	1.0	0

The *atomic weight* of each element is simply a way of comparing the mass of the atoms of that element with the mass of an arbitrary standard, the carbon atom. A scale of relative atomic weights based on the atomic mass unit (amu) has been established by the scientific community. The amu is defined as exactly 1/12 of the mass of an atom of carbon-12, which is a carbon atom with an atomic weight of 12.0000.

On this scale, the atomic weight of hydrogen (H) is 1.0 amu, that of helium (He) is 2.0 amu, and that of magnesium (Mg) is 24.3 amu. This tells us that He atoms have twice the mass of H atoms, while Mg atoms are about 24 times heavier than H atoms.

Figure 1.1 shows an idealized arrangement of the protons, neutrons and electrons in these atoms. The protons and neutrons reside in the nucleus, with electrons orbiting about the nucleus like a tiny solar system.

Appendix 1 gives the atomic weight of selected elements. Atomic weights are normally given to four decimal places, but they are rounded off to one decimal place for convenience in chemical calculations. This is sufficiently accurate for most purposes.

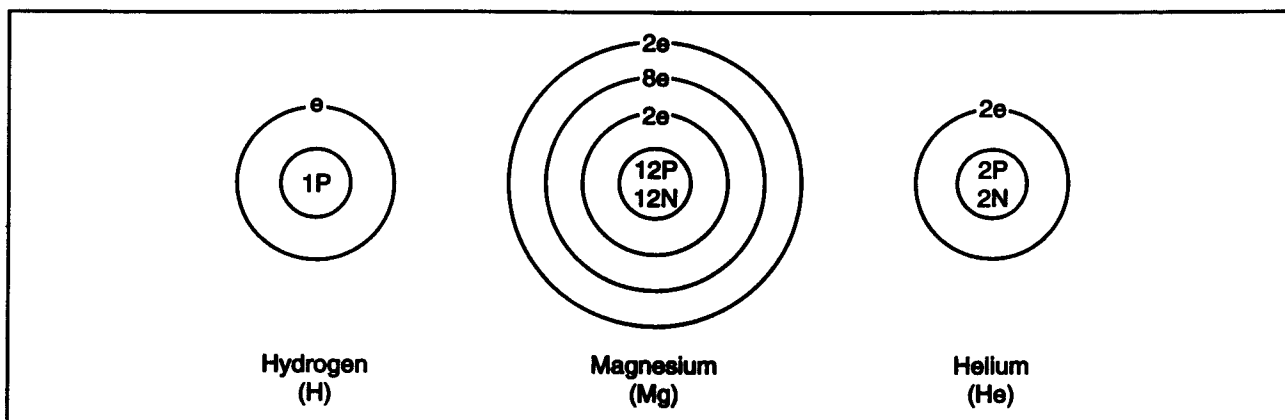


Figure 1.1 Hydrogen, Magnesium and Helium Atoms

Isotopes

As previously stated, electrons have a negligible weight as compared to protons and neutrons. Since protons and neutrons have unit mass, it follows that the atomic weights of atoms should be whole numbers if we neglect the very small mass due to the electrons. An examination of the atomic weights given in Appendix 1 shows that many of the elements have atomic weights which deviate considerably from whole numbers. For example, chlorine has an atomic weight of 35.5 and iron an atomic weight of 55.8.

Careful study has shown that most elements are actually mixtures of two or more forms of the element. Chlorine, for example, has been found to be made up of two kinds of chlorine, one of which has an atomic weight of 35 and the other of 37. In ordinary chlorine these two species are mixed in such a proportion as to give the average atomic weight of 35.5. The two kinds of chlorine have the same chemical properties but the mass of their atoms is different. They both have 17 electrons and 17 protons.

However, the atom of atomic weight 35 has 18 neutrons while the atom of atomic weight 37 contains 20 neutrons. In reality we have the same element, chlorine, in both instances. Elements with the same number of protons but different atomic weights are called *isotopes*. Thus, ordinary chlorine is a mixture of two isotopes. Many other elements are also mixtures of isotopes, so their atomic weights are actually average weights based on the mixture of isotopes which normally exist in the naturally occurring element.

MOLECULES AND MOLECULAR WEIGHTS

Atoms combine to form *molecules*, which can be defined as the smallest particle of a compound which can exist. Thus, atoms have the same relation to elements as molecules have to compounds.

A molecule of a compound is formed by the union of two or more atoms of the elements of which the compound is composed. The *molecular weight* (or formula weight) is the relative mass of a single molecule compared to the mass of the carbon-12 atom. Molecular weight is found by adding the atomic weights of the elements which form the molecule. An example calculation is shown in Table 1.3.

TABLE 1.3
Calculation of Molecular Weight

Compound	Constituent Elements	Number of Atoms	Atomic Weight	Wt. of Element Present
H ₂ O	H	2	1	2 amu
	O	1	16	16 amu
Molecular Weight of H ₂ O = Total =				18 amu

Molecular weights, like atomic weights, are also relative weights. A molecular weight of 18 means that one molecule of water is 18 ÷ 12, or 1.5 times as heavy as one atom of carbon.

Another example: The chemical formula for sulfuric acid is H₂SO₄, which means that it contains 2 atoms of hydrogen, 1 atom of sulfur and 4 atoms of oxygen. Therefore, its molecular weight is:

$$(2 \times 1) + 32 + (4 \times 16) = 98$$

It should be noted that the traditional terms *atomic weight* and *molecular weight* are used herein even though they have been replaced by the terms *relative atomic mass* and *relative molecular mass* in the SI metric system of units.

Attempts to measure the mass of an individual atom didn't work out too well because atoms are far too small to be seen or weighed individually; the smallest bit of matter that can be reliably measured contains an enormous number of atoms. We deal with large numbers of atoms in real situations, and a unit called the mole has been adopted as a standard unit of measurement.

A mole is defined as the amount of substance that contains as many *elementary entities* (atoms, molecules, or other particles) as there are atoms in 0.012 kg (12 g) of pure carbon-12 isotope. It is a fundamental SI unit and is abbreviated “mol” for use in equations.

According to this definition, one mole refers to 6.02×10^{23} “elementary entities” whose identities must be specified. We could have a mole of atoms or a mole of molecules (or a mole of ions, electrons, or other particles). For that matter we could have a mole of Lincoln Town Cars or BMW’s.

The mass of one mole of atoms of a pure element is numerically equal to the atomic weight of that element (in amu's), expressed in grams. For example, 1 mole of elemental sodium contains 6.02×10^{23} sodium atoms and has a mass of 23.0 grams.

Similarly, one mole of ions contains 6.02×10^{23} ions, and this number of ions has a mass equal to the atomic or formula mass expressed in grams. Hence, one mole of Mg^{++} contains 6.02×10^{23} magnesium ions, and has a mass of 24.3 grams.

Another example: If you obtain a sample of pure gold, which has an atomic weight of 197 amu, and weigh out 197 grams, you will have one mole of gold, which contains 6.02×10^{23} atoms of gold. Thus, one atom of gold weighs:

[illegible]

When dealing with gases, you have to be careful, since some gases exist as atoms while others exist as molecules containing two atoms. Helium exists as discrete He atoms, so one mole of helium consists of 6.02×10^{23} atoms, and has a mass of 2.0 grams. Oxygen commonly exists as O_2 molecules (containing two atoms of oxygen), so one mole of oxygen has a mass of 32.0 grams contains 6.02×10^{23} molecules. This concept is further illustrated in Table 1.4.

Unless otherwise stated, the mass contained in a mole is expressed in grams. However, moles can also be expressed in other units, such as pounds, tons, or kilograms for the sake of convenience.

TABLE 1.4
Mass of One Mole of Atoms of Some Common Elements

Element	Sample Mass	Contains
Carbon	12.0 g of C	6.02×10^{23} or 1 mole of C atoms
Calcium	40.0 g of Ca	6.02×10^{23} Ca atoms or 1 mole of Ca atoms
Hydrogen	1.0 g of H ₂	6.02×10^{23} H atoms or 1 mole of H atoms = 3.011×10^{23} H ₂ molecules or 0.5 mole of H ₂ molecules
Nitrogen	14.0 g of N ₂	6.02×10^{23} N atoms or 1 mole of N atoms = 3.011×10^{23} N ₂ molecules or 0.5 mole of N ₂ molecules
Sulfur	32.0 g of S ₈	6.02×10^{23} S atoms or 1 mole of S atoms = 0.753×10^{23} S ₈ molecules or 0.125 mole of S ₈ molecules

Using carbon as an example:

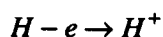
- 1 mol C = 12 g
- 1 lb-mole C = 12 lb. 12 lb = 5448 g which equals 454 g-mol
- 1 ton-mole C = 12 tons. 12 tons = 24000 lb which is 2000 lb-mol or 908000 g-mol

Although grams are convenient for a laboratory chemist, we often use larger units in industrial process calculations because of the large quantities involved.

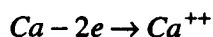
IONS AND VALENCE

As previously stated, atoms are made up of protons, neutrons, and electrons. Each atom has an equal number of protons and electrons, so their charges balance out and the net charge is zero. If, however, an atom should lose or gain electrons, an imbalance in charge will result since the number of protons in the nucleus stays constant. Therefore, if an atom gains electrons it will have a net negative charge. If it loses electrons it will have a net positive charge. Whenever this happens, the atom is no longer called an atom. It becomes an *ion* which may be defined as an atom or group of atoms containing an electric charge. A positively charged ion is called a *cation* while a negatively charged ion is called an *anion*.

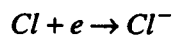
The amount of charge is called the *valence* and is a measure of the element's chemical combining power. When hydrogen ionizes it loses its electron and has a net positive charge or valence of +1.



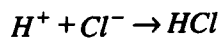
Calcium ionizes by losing 2 electrons and thus the calcium ion has a valence of +2.



Chlorine ionizes by gaining 1 electron and the chlorine ion has a valence of -1.

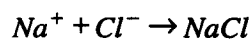


Hydrogen is taken as the standard with a valence of +1. Any atom or group of atoms that combines with hydrogen on a one-to-one basis will also have a valence of one. The formula of hydrochloric acid, HCl, tells us that one atom of hydrogen combines with one atom of chlorine. Thus the valence of chlorine is also one; although it is a negative 1 (-1). The sum of the valences must be zero since compounds have a net charge of zero.



$$(+1) + (-1) = 0$$

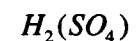
Similarly, for table salt:



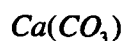
$$(+1) + (-1) = 0$$

Radicals

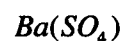
A **radical** is a group of atoms found in certain compounds which reacts as a unit, i.e., as if it were a single atom or ion. The radicals in the compounds following are enclosed in parentheses. Each radical shown has a valence of -2 .



Sulfuric Acid



Calcium Carbonate



Barium Sulfate

If these compounds were ionized we would find that the radicals behave as polyatomic anions:



Sulfate ion



Carbonate ion

EQUIVALENT WEIGHTS

When elements combine to form a given compound they do so in a fixed and invariable ratio by weight. This ratio can be predicted by means of equivalent weights. For an **element** or **ion**:

$$\text{Equivalent Weight} = \frac{\text{Atomic Weight}}{\text{Valence}} \quad (1.1)$$

Since equivalent weights are positive, the equivalent weight of an anion is calculated by dividing the atomic weight by the absolute value of the valence.

It should be remembered that an atom of an element exhibits no charge. Therefore, the valence of an element is actually the charge it exhibits when it is ionized.

Some elements, such as iron, have more than one equivalent weight because it can exist in more than one valence state. For example, iron has two different equivalent weights because it can exist as either ferrous ions (Fe^{++}) or ferric ions (Fe^{+++}).

The equivalent weight of a **compound** is:

$$\text{Equivalent Weight} = \frac{\text{Molecular Weight}}{\text{Net Positive Valence}} \quad (1.2)$$

A compound has no charge. The net positive valence of a compound is the total number of positive charges that would result if the compound were ionized in an aqueous solution.

Example 1.1: Determine the net positive valence of the following compounds: NaCl, K₂CO₃, CaSO₄ and Fe₂(SO₄)₃.

To determine the net positive charge, first write down the formulas of the compounds. Then assume that the compound has ionized in water. Split the cations from the anions as follows:



Then consider the positive (left) part of the formula. Multiply the valence of the positive part times the number of ions to obtain the net positive valence.



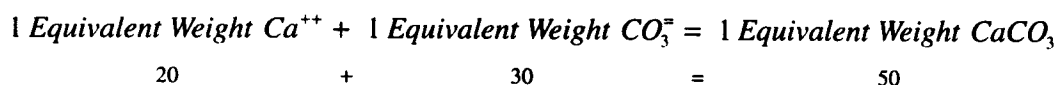
Net Positive Valence = Valence of positive element multiplied by the number of ions

Using Equivalent Weights

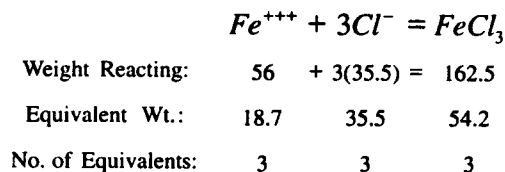
One of the main uses of equivalent weights is to permit us to easily determine the quantity of reactants and products in a chemical reaction.

If two elements, A and B, combine to form compound C, they will do so on an equivalent basis. One equivalent of A will combine with one equivalent of B to form one equivalent of C.

For example:



Similarly, for ferric chloride:



We see that one atomic weight of iron has combined with three atomic weights of chlorine to give one mole of FeCl₃. More important, however, 3 equivalents of iron have combined with 3 equivalents of chlorine to give 3 equivalents of ferric chloride. Equivalents always combine on a one-to-one basis. That is the reason we use them.

Some examples of equivalent weights are given in Table 1.5.

A more complete list of equivalent weights of selected ions and compounds is given in Appendix 2.

TABLE 1.5
Equivalent Weights

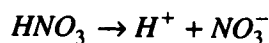
Element, Ion or Compound	Atomic or Molecular Weight	Valence	Equivalent Weight
H	1	+1	1
O	16	-2	8
CO ₃ ⁼	60	-2	30
SO ₄ ⁼	96	-2	48
Ca ⁺⁺	40	+2	20
Fe ⁺⁺ (Ferrous ion)	56	+2	28
Fe ⁺⁺⁺ (Ferric ion)	56	+3	18.7
CaCO ₃	100	+2*	50
HCl	36.5	+1*	36.5
Cl	35.5	-1	35.5

* The compound itself has no valence. This is the total valence of the cations if the compound were ionized in an aqueous solution.

ACIDS, BASES AND SALTS

Acids

An acid is any substance that is capable of giving up hydrogen ions. Acids neutralize bases to yield salts and water, and they ionize or dissociate in water. The ionization of nitric acid in water is given as follows:



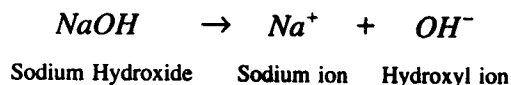
Some common acids are listed in Table 1.6.

TABLE 1.6
Common Acids

Acid	Symbol
Hydrochloric	HCl
Carbonic	H ₂ CO ₃
Sulfuric	H ₂ SO ₄
Nitric	HNO ₃
Phosphoric	H ₃ PO ₄

Bases

Bases are substances which accept hydrogen ions in a chemical reaction. A base is commonly defined as being a substance that dissociates when dissolved in water to yield hydroxyl ions. For example:



Salts

A salt is an ionic compound containing a positive ion other than the hydrogen ion and a negative ion other than the hydroxyl or the oxide ion.

SOLUTIONS

Solutions are homogeneous mixtures of two or more substances. They are like compounds in that they are homogeneous and like mixtures in that the relative proportions of the constituents are variable.

A solution is formed when sugar is dissolved in water. It is perfectly uniform or homogeneous; if we should taste samples taken from various parts of the solution, we would find that each part has the same degree of sweetness. The amount of sugar we can dissolve in 100 milliliters of water is variable; we may dissolve one gram, ten grams, or sixty grams of sugar in the water. There is a limit, though, to the amount of sugar we can dissolve in a given amount of water at a certain temperature. This limiting amount is termed the **solubility** of sugar in water at that temperature.

TABLE 1.7

Properties of Mixtures, Solutions and Compounds

Mixtures	Solutions	Compounds
Not always homogeneous	Homogeneous	Homogeneous
Variable proportions of constituents	Variable proportions of constituents	Fixed proportions of elements

The dissolved material in a solution (in this case sugar) is called the **solute**. The water is the dissolving medium in this particular example and is called the **solvent**. Likewise, if we dissolve salt in water, we create a solution called **brine** — salt is the solute and water is the solvent.

It should be realized that there are several types of solutions which may be formed when different materials are added to water.

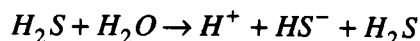
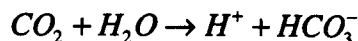
The dissolving of sugar in water is an illustration of a solution where the individual solute molecules disperse themselves uniformly throughout the solvent. The solid sugar is said to be **molecularly dispersed**.

Most of the materials of interest to us in water chemistry are materials which **ionize** when added to water. Thus when table salt is added to distilled water, the solid crystals of NaCl dissolve and break up into sodium (Na^+) and chloride (Cl^-) ions.

Most water contains considerable quantities of different dissolved impurities which exist as ions. Thus, a water analysis is really just a list of the types and amounts of the different ions which are present in the water of interest. Remember ... pure water contains only hydrogen and oxygen.

One other very important type of solution in industrial water chemistry is one where a gas is dissolved in water. The three gases of greatest interest in the oilfield are oxygen, carbon dioxide, and hydrogen sulfide. The primary problem associated with these gases is that they tend to make the water more corrosive. Thus, we are usually quite interested in knowing the amount of dissolved gases, as well as the amount of other impurities, present in a given water sample.

Oxygen dissolves in water as an oxygen molecule, O_2 . Carbon dioxide (CO_2) and hydrogen sulfide (H_2S) partially ionize when they dissolve in water, resulting in a mixture of dissolved gas molecules and ions.



The relative amounts of CO_2 and HCO_3^- , or H_2S and HS^- in the water are dictated by the pH of the water.

Carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are also known as **acid gases** because they create hydrogen ions (H^+) when they dissolve in water, thus making the water more acid.

Methods of Expressing Concentrations

When discussing solutions it is necessary to define the quantity of the different solutes present in the solvent. The amount of solute present is expressed as some fraction of the amount of solvent or total solution. It is called the **concentration** and may be expressed in a number of ways.

Weight of Solute per Volume of Solution

Most solutes in water are present in rather small quantities and so concentrations are usually expressed in milligrams of solute per liter of solution (mg/L).

Parts per Million

A dimensionless concentration term which expresses the number of unit weights of solute per million unit weights of solution (ppm).

One ppm is equivalent to 1.0 mg of solute per 1 000 000 mg (1000 g) of solution.

$$ppm = \frac{mg/L}{S.G.} \quad (1.3)$$

Where: S.G. = specific gravity (relative density)

Molarity

A one molar solution contains one gram-molecular weight of solute in a liter of solution. The molecular weight of table salt (NaCl) is 58.4 g. A one molar solution of table salt in water contains 58.4 grams of NaCl per liter of solution.

$$\frac{Moles}{Liter} = \frac{mg/L}{1000 \times MW} \quad (1.4)$$

Where: MW = g-molecular wt

Molality

A one molal solution contains one gram-molecular weight of solute in 1000 g (1.0 kg) of solvent. A one molal solution of table salt contains 58.4 g of NaCl in 1000 g of water.

$$\text{Molality} = \frac{\text{Moles}}{1000gH_2O} = \frac{\text{mg/L}}{1000(1000 \times S.G. - TDS + 1000)} \quad (1.5)$$

Where: TDS = Total dissolved solids (See Chapter 2.)
 S.G. = Specific gravity (relative density).

Normality

A one normal solution contains one gram equivalent weight of solute in a liter of solution. Since the molecular weight and the equivalent weight of table salt are the same, a one normal solution is the same as a one molar solution. It contains 58.4 grams of salt per liter of solution. If the solute were sulfuric acid (H_2SO_4), however, a one normal solution would contain 49 g of H_2SO_4 per liter of solution. This results from the fact that the molecular weight of H_2SO_4 is 98 and its equivalent weight is $98 \div 2 = 49$. In this case a one-molar solution would contain one gram molecular weight of H_2SO_4 (98 g), while a one-normal solution would contain one gram-equivalent weight (49 g).

Standard Solutions

Standard solutions are simply solutions of known composition.

pH

The pH of a water is the logarithm of the reciprocal of the hydrogen ion concentration expressed in moles per liter.

$$pH = \frac{1}{[H^+]} \quad pH = \log \frac{1}{[H^+]} \quad (1.6)$$

It is also a number between 0 and 14, indicating the degree of acidity or alkalinity. The pH scale is similar to that of a thermometer. Just as a thermometer measures heat intensity, the magnitude of the pH indicates the intensity of acidity or alkalinity.

The midpoint of the pH scale is 7; a solution with this pH is neutral. Numbers below 7 denote acidity; those above alkalinity. Since pH is a logarithmic function, solutions having a pH of 6.0, 5.0, and 4.0 are 10, 100 and 1000 times more acid than one with a pH of 7.0. Just remember that hydrogen ions (H^+) make a solution acid and therefore force the pH toward zero. Hydroxyl ions (OH^-) make a solution basic or alkaline and push the pH upward.

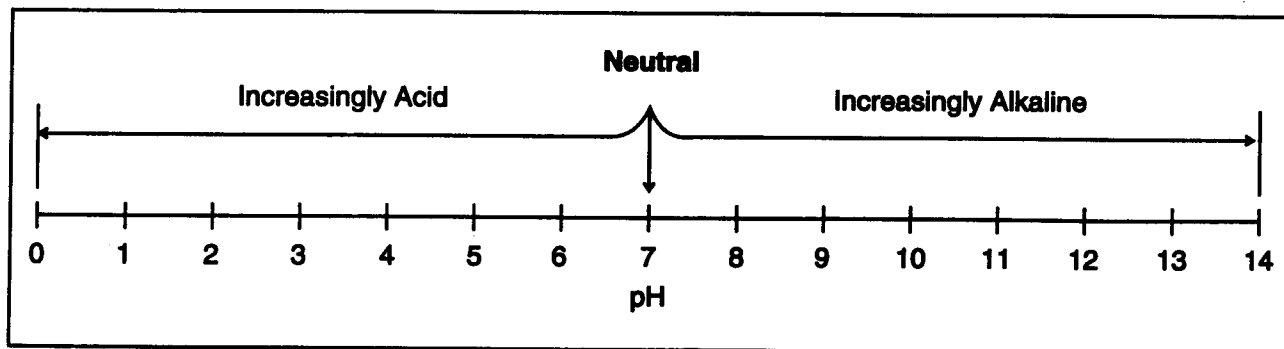


Figure 1.2 pH Scale

SYSTEM OF MEASUREMENT

Chemical calculations traditionally have used the metric system because it is relatively simple; all measures are expressed in multiples of ten. However, several years ago the international scientific community switched from traditional metric to the Systeme Internationale, or SI metric. The basic units are given in Table 1.8.

TABLE 1.8
Basic SI Units

Quantity	Traditional Metric	SI Metric
Mass	gram (g)	kilogram (kg)
Length	centimeter (cm)	meter (m)
Time	second (s)	second (s)
Volume	cubic centimeter (cm ³) or liter (L)	cubic meter (m ³)

There also is a clarification of the words “weight” and “mass” which have been used traditionally as synonyms (incorrectly). In addition, there is clarification of the term “mole,” expressed in symbol form as “mol,” as noted in a previous section.

Prefixes

A system of prefixes is used to denote the size of a unit as shown in Table 1.9.

TABLE 1.9
SI Prefixes

Multiplication Factor	SI Prefix	SI Prefix Symbol	Meaning (USA)	Meaning (Some Other Countries)
1 000 000 000 000 000 000 = 10 ¹⁸	exa	E	one quintillion times	trillion
1 000 000 000 000 000 = 10 ¹⁵	peta	P	one quadrillion times	thousand billion
1 000 000 000 000 = 10 ¹²	tera	T	one trillion times	milliard
1 000 000 000 = 10 ⁹	giga	G	one billion times	
1 000 000 = 10 ⁶	mega	M	one million times	
1 000 = 10 ³	kilo	k	one thousand times	
100 = 10 ²	hecto	h	one hundred times	
10 = 10	deka	da	ten times	
0.1 = 10 ⁻¹	deci	d	one tenth of	
0.01 = 10 ⁻²	centi	c	one hundredth of	
0.001 = 10 ⁻³	milli	m	one thousandth of	
0.000 001 = 10 ⁻⁶	micro	μ	one millionth of	
0.000 000 001 = 10 ⁻⁹	nano	n	one billionth of	milliardth
0.000 000 000 001 = 10 ⁻¹²	pico	p	one trillionth of	billionth
0.000 000 000 000 001 = 10 ⁻¹⁵	femto	f	one quadrillionth of	thousand billionth
0.000 000 000 000 000 001 = 10 ⁻¹⁸	atto	a	one quintillionth of	trillionth

Length (Distance)

These prefixes normally are shown in front of the meter, the standard length unit. So,

$$1 \text{ millimeter (mm)} = 0.001 \text{ meter (m)}$$

$$1 \text{ centimeter (cm)} = 0.01 \text{ m}$$

$$1 \text{ decimeter (dm)} = 0.1 \text{ m}$$

Common conversions are:

$$1 \text{ inch} = 2.54 \text{ cm} = 0.0254 \text{ m}$$

$$1 \text{ mil} = 0.001 \text{ inch} = 25.4 \text{ micrometer } (\mu\text{m}) = 25.4 \text{ microns}$$

$$1 \text{ meter} = 39.37 \text{ inches}$$

Volume

The term liter (or litre) is not an official part of the SI system but is acceptable as a term for the cubic decimeter (dm^3). It is abbreviated as "L" rather than the lower case "l" to prevent confusion with the numeral "1".

$$1 \text{ cubic meter (m}^3\text{)} = 1000 \text{ dm}^3 = 1000 \text{ L}$$

$$1 \text{ liter (L)} = 1000 \text{ milliliters (mL)} = 1.06 \text{ quarts}$$

The term "cc" or cubic centimeters is discouraged; use mL instead. They are equivalent for ordinary usage.

Mass

Some multiple of a gram (g) is used as the most common mass unit. A very common concentration term is milligrams per liter (mg/L).

$$1 \text{ kg} = 1000 \text{ g} = 2.205 \text{ lb}$$

$$1 \text{ lb} = 453.5 \text{ g}$$

The term *specific gravity* (or *relative density*) is the density of a material in mass per unit volume divided by the of pure water at the same conditions. The SI metric system uses "relative density" instead of the more traditional "specific gravity." The most common abbreviations are S.G. or @.

Temperature

The temperature normally is expressed in degrees centigrade or degrees Celsius ($^{\circ}\text{C}$) when the metric system is employed. This may be compared to degrees Fahrenheit ($^{\circ}\text{F}$) as shown in Figure 1.3.

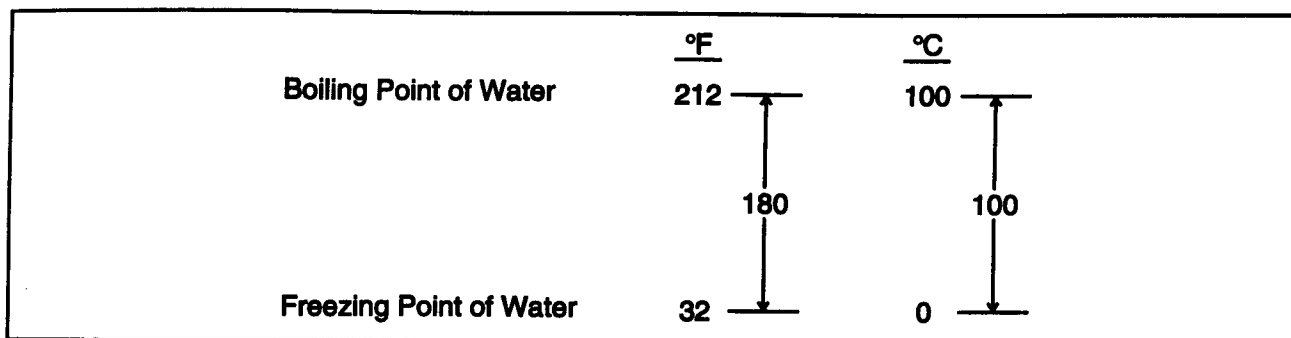


Figure 1.3 Comparison of Fahrenheit and Centigrade

Formulas for converting temperatures from one scale to the other are:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32 \quad (1.7)$$

$$^{\circ}\text{C} = \frac{1}{1.8} \times (^{\circ}\text{F} - 32) \quad (1.8)$$

A conversion chart is given in Appendix 4.

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- 1.4 Hess, F. C.: *Chemistry Made Simple*, Doubleday & Company, Inc., Garden City, New York (1984).

2

WATER SAMPLING AND ANALYSIS

Many profound statements can be made about water and its importance in our lives. Its beneficial qualities are many. However, routinely handling large quantities of waters of vastly differing compositions at minimum cost and with a minimum of operating problems often presents some tremendous problems.

CHEMICAL AND PHYSICAL PROPERTIES

Water is often called the universal solvent because it has the power to dissolve virtually all inorganic substances to some extent. In its pure state it has the following physical properties:

TABLE 2.1
Physical Properties of Water

Property	Value
Molecular Weight	18
Density @ 4°C	1 g/mL
Freezing Point	32°F [0°C]
Boiling Point	212°F [100°C]

Most water handling problems in the oilfield arise from the fact that water is such a superb solvent. Both produced waters and surface waters contain considerable quantities of impurities. It has had ample contact with soil and rock formations and has dissolved certain compounds. In addition, it usually contains some suspended solids and dissolved gases. Water will dissolve metal. Microbiological growths often proceed very readily in water. As conditions of temperature and pressure change, many of the dissolved compounds may become insoluble to some degree, precipitate from the water and form scale. The number and combination of difficulties which may arise in water handling are enormous.

In the oilfield we use water for many purposes. The most common are:

- Injection into subsurface formations to increase oil recovery and/or maintain reservoir pressure.
- Injection into subsurface formations to dispose of waste waters.
- Disposal of waste waters into surface waters.

- Cooling of natural gas engine jackets, compressor cylinders, natural gas and other process streams.
- Feedwater for boilers and steam generators.

Regardless of the application, we have two primary goals from an operational standpoint:

- Avoid plugging and deposition of solids in lines, vessels and wells.
- Prevent corrosion of surface and downhole equipment.

WATER SAMPLING

One of the first items of interest in water handling is to sample it and determine its composition. This is our primary means of detecting present and potential problems. However, the water sample must be representative of the water of interest or our analysis will lead to false conclusions. The importance of good sampling practices cannot be overemphasized. An extremely accurate chemical analysis of a water sample, followed by a brilliant assessment of the problems indicated by the analysis, is worthless if the sample does not represent the water in your system.

Sample Containers

Clean (preferably new) plastic bottles with tightly fitting plastic caps are recommended for routine water samples. Pint or quart (500 mL or one liter) bottles are commonly used. Several different types of plastic and different cap designs are available. Once you have selected a particular bottle and cap combination, fill it with water, cap it, and squeeze it to make sure that the cap will not pop off or leak. Wide-mouth bottles are usually easier to fill, but often have less dependable caps.

Label the bottle (not the cap) so that the sample can be identified. Cardboard mailing tubes or cartons should be obtained if the samples are to be shipped to a laboratory or carried a considerable distance.

If the sample is to be analyzed for oil content or for the concentration of any other organic constituent, a glass bottle should be used. Oil or other organic materials will adhere to the walls of a plastic container or be absorbed by it. Extra precautions are necessary in packing the sample for shipment. Freezing can be a problem. Use a plastic cap with a plastic liner.

Never use a metal container or a metal cap. The water will corrode them and become contaminated with corrosion products.

Sample Volume

A minimum sample volume of one pint (500 mL) is recommended for routine analysis.

If you are going to personally perform on-site analyses, you can take as much as you think you need. If only one or two analyses are to be performed, only a few hundred milliliters may be necessary. Also, since you are on site, you can run back to the sampling point and obtain some more water (provided the water system is not changing composition rapidly). But remember that if you send water samples to a laboratory several miles away and you don't send enough to permit them to perform all of the analyses you want, you are simply out of luck. Always send more than enough if there is any doubt in your mind as to the minimum volume required.

Sampling Procedure

If a sampling valve is available, connect a piece of plastic tubing to the end of the valve. A small nipple or hose connector is handy for this purpose. Open the valve and let the water run for at least one minute. Watch to see if the color of the water is changing. If it is, wait until the color becomes constant. Remember that there is probably some debris in the valve or in the bottom of the line and this will have to be flushed out before you can get a good sample.

Once you have a representative water flow, the following sampling procedures are recommended:

- **Sample for Routine Analysis** — Rinse the bottle out three times, then place the end of the hose in the bottom of the bottle and let the bottle overflow for an estimated 10 volumes. Then slowly pull out the hose and quickly cap it to minimize (1) oxygen contamination and (2) the escape of dissolved gases.
- **Sample for Oil-in-Water Analysis** — Fill a clean glass bottle to the neck directly from the sample point and cap quickly. Do not rinse or overflow the bottle with the water to be sampled as in the case of the sampling procedure given for routine analyses. Oil will tend to adhere to the bottle wall and separate from the water. If the bottle is filled more than once, oil from each filling is likely to stay in the bottle, giving erroneously high results. Alternately, free oil may be carried out of the bottle by overflowing, giving low results.
- **Sample for Bacterial Analysis** — This procedure is covered in detail in Chapter 5.

Once the sample is capped, prepare a label immediately and attach it to the bottle or label the bottle with an indelible, smear-proof marking pen. Make sure the label is securely glued to the bottle. You can mark the cap for convenience if you wish, but remember that caps can be inadvertently switched!

If the sample is to be sent to a laboratory for analysis it should be accompanied by a Water Sample Description Form detailing the sampling conditions. A typical example is given in Appendix 5.

Some other hints:

1. Take wellhead samples at the wellhead, not at the heater-treater or at the tank.
2. If a tank is to be sampled, sample it at several levels, preferably top, middle and bottom. This can require special equipment. You may be able to borrow a "thief" from a gauger and clean it thoroughly before use in order to obtain a sample from the center of a conventional tank.
3. Take samples from the system when it is operating normally. It is often most convenient to take samples when the system is shut down. Needless to say, this type of sample is of questionable value. Make sure the flow rate is "normal" and that nothing unusual is going on upstream of the sampling point.
4. If you are sampling a surface water as a possible source for a waterflood remember that the water composition (especially the turbidity, oxygen concentration and microbial population) may change considerably with the time of the year. It is advisable to sample at several points over a period of several months.
5. Waters for disposal may change considerably with time. Plant waste waters may show a cyclic change in composition due to ion exchange regeneration, cooling tower blowdown cycles, or plant cleaning operations. Once again, a series of samples over a period of time is recommended. Conversations with plant personnel may enrich your intuition as to when to take samples which will reflect the greatest variations in disposal water composition. This can influence your water treating procedure.

QUANTITATIVE ANALYSIS OF OILFIELD WATERS

Water analyses are routinely carried out in laboratories by skilled chemists. They are capable of making extremely accurate measurements on the water sample provided. However, many water properties can change very quickly after sampling. Typical are pH, temperature, dissolved gas content, suspended solids and bacterial population. This means that many of the properties which are of greatest concern to us can be determined accurately only by measuring them on-site. Therefore, a thorough analysis of any water usually involves both laboratory and field analyses.

It is extremely important that any person involved in a water injection or disposal project have an understanding of:

- The constituents and properties of water of greatest importance in water systems
- The significance of each
- The analytical methods typically used, along with their strengths and weaknesses

If these items are understood, then it is possible to specify which analyses are needed and to understand the significance of the results.

Primary Constituents and Properties

In water handling operations we are primarily concerned with those ions and physical properties which are important from the standpoint of plugging or corrosion. Table 2.2 is a list of the most important.

It may also be desirable to measure the amount of chlorine (a bactericide) or the concentration of treating chemicals present in order to monitor their effectiveness.

In steam operations and cooling water systems the amount of silica (SiO_2) in the water is also important, as it can form deposits.

TABLE 2.2
Primary Constituents and Properties of Oilfield Waters

Cations	Anions	Other Properties
Sodium (Na^+)	Chloride (Cl^-)	pH
Calcium (Ca^{++})	Sulfate (SO_4^{--})	Bacterial Population
Magnesium (Mg^{++})	Bicarbonate (HCO_3^-)	Suspended Solids: Amount, size, shape, composition
Iron (Fe^{+++} & Fe^{++})	Carbonate (CO_3^{--})	Turbidity
Barium (Ba^{++})		Water Quality
Strontium (Sr^{++})		Dissolved Oxygen
		Dissolved Carbon Dioxide
		Total Sulfides as H_2S
		Oil Content
		Temperature
		Total Dissolved Solids (TDS)
		Specific Gravity
		Resistivity (Conductivity)
		Silica

Significance of Constituents and Properties^(2.1)

Cations

- a. **Sodium** is a major constituent in oilfield waters, but does not normally cause any problems. About the only exception is the precipitation of NaCl from extremely salty brines.
- b. The **calcium** ion is a major constituent of oilfield brines and may run as high as 30 000 mg/L although its concentration is normally considerably lower. The calcium ion is of major importance because it readily combines with bicarbonate, carbonate or sulfate ions and precipitates to form adherent scales or suspended solids.
- c. **Magnesium** ions are usually present in much lower concentrations than calcium. They tend to **add** to CaCO₃ scaling problems by co-precipitating with the calcium ion. It is very common to find magnesium in calcium carbonate scales.

Magnesium ions **decrease** the amount of CaSO₄, CaSO₄ and CaSO₄ scales. They do so by forming "ion pairs" with the sulfate ion. Essentially, the magnesium ion has the ability to form a compound which remains in solution. The sulfate ions which are tied up with magnesium are not available to form sulfate scales.

- d. The natural **iron** content of formation waters normally is quite low and its presence is usually indicative of corrosion. It may be present in solution as ferric (Fe⁺⁺⁺) or ferrous (Fe⁺⁺) ions, or it may be in suspension as a precipitated iron compound. "Iron counts" are often used to detect and monitor corrosion in a water system. The presence of precipitated iron compounds is one of the major causes of formation plugging.
- e. **Barium** is of importance primarily because of its ability to combine with the sulfate ion to form barium sulfate, which is extremely insoluble. Even small quantities can present severe problems.
- f. **Strontium**, like barium and calcium, can combine with the sulfate ion to form insoluble strontium sulfate. Although more soluble than barium sulfate, it is often found in scales mixed with barium sulfate.

Anions

- a. The **chloride** ion is nearly always the major anion in produced brines and is usually present as a major constituent in fresh waters. The major source of the chloride ion is NaCl, so the chloride ion concentration is used as a measure of water salinity.

Although salt deposition can be a problem, it is normally of little consequence. The primary problem associated with the chloride ion is that the corrosivity of the water increases as it gets saltier. Therefore, high chloride concentrations make corrosion more likely. Also, the chloride ion is a stable constituent and its concentration is one of the easier ways of identifying a water.

- b. The **sulfate** ion is a problem because of its ability to react with calcium, barium or strontium to form insoluble scales. It also serves as a "food substance" for sulfate reducing bacteria.
- c. The **bicarbonate** ion can react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. It is present in virtually all waters. Bicarbonate ion concentration is sometimes called methyl orange alkalinity.
- d. Like the bicarbonate ion, the **carbonate** ion can also react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. Carbonate ions are rarely present in

produced waters because the pH is usually too low (< 8.3). Carbonate ion concentration is sometimes called phenolphthalein alkalinity.

Other Properties

- a. The **pH** is extremely important for several reasons. The solubility of CaCO_3 and iron compounds is highly dependent on pH. The higher the pH, the greater the tendency for precipitation.

As the pH decreases (becomes more acidic) the scaling tendency of the water is decreased, but its corrosivity is increased. Most oilfield waters have a pH between 4 and 8.

Both H_2S and CO_2 are “acid” gases as they tend to lower the pH of water (make it more acid) when they dissolve in water. They partially ionize when they dissolve and the degree of ionization is reflected by the pH. This is important in predicting their effect on corrosion and suspended solids.

Since pH values usually change rapidly after a sample is withdrawn from a pressurized system (due to the escape of dissolved acid gases), pH values should be measured immediately after the sample is taken.

- b. The presence of **bacteria** may result in corrosion and/or plugging. A more detailed treatment of this subject is given in Chapter 5.
- c. The quantity of **suspended solids** which can be filtered from a given volume of water using a membrane filter is one basis for estimating the plugging tendency of a water. A $0.45\ \mu\text{m}$ pore-size filter is commonly used.
- d. It is possible to estimate the **particle size distribution** of the suspended solids in a water sample by various techniques. A knowledge of the particle size distribution can be very helpful in determining the need for filtration and in filter selection. It is also useful in monitoring filter performance.
- e. Determination of **particle shape** by visual or scanning electron microscopy is very helpful in the determination of filtration needs. It is usually used in conjunction with particle size distributions.
- f. Determination of the **composition of the suspended solids** makes it possible to ascertain their origin (corrosion products, scale particles, formation sand, etc.) so that proper remedial action can be taken. Knowledge of their chemical composition is also important from the standpoint of designing a cleanout procedure should plugging occur.
- g. **Turbidity** simply means that the water is not “clear” and that it contains undissolved matter such as suspended solids, dispersed oil or gas bubbles. It is a measure of the degree of “cloudiness” of the water. Turbidity indicates the possibility of formation plugging in injection operations. Turbidity measurements are often used to monitor filter performance.
- h. **Water quality** is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of $0.45\ \mu\text{m}$ is most commonly used. The utility of water quality testing lies largely in its use as a comparative measurement.
- i. **Dissolved oxygen** contributes significantly to the corrosivity of a water. Also, if dissolved iron is present in a water, the entry of oxygen into the system can result in the precipitation of dissolved iron as insoluble iron oxides which may result in plugging. Oxygen also facilitates the growth of aerobic bacteria.

- j. *Dissolved carbon dioxide* influences the pH, corrosivity and CaCO_3 scaling tendency of a water.
- k. The presence of *sulfides* in water will increase its corrosivity. Dissolved sulfides exist in water as a mixture of HS^- ions and dissolved H_2S gas at the pH values normally found in oilfield waters, and the total concentration of both species is usually measured and referred to as “total sulfides”. It may be present naturally in the water or it may be generated by sulfate-reducing bacteria. If a normally sweet (free of H_2S) water begins to show traces of H_2S , this indicates that sulfate-reducing bacteria are probably at work somewhere in the system busily corroding holes in your piping and vessels. In addition, iron sulfide will be generated as a corrosion product, and it is a very efficient plugging agent.
- l. The presence of dispersed or emulsified *oil* in water often presents problems when injecting produced waters.

Oil in water can cause decreased injectivity in several ways. It can cause “emulsion blocks” in the formation. It serves as an excellent glue for certain solids, such as iron sulfide, thereby increasing their plugging efficiency.

When water is being injected into an aquifer with no initial oil saturation, oil in the water can be trapped in the pores of the formation rock around the wellbore. This creates an oil saturation, which can reduce injectivity.

An analysis for oil content should be conducted on any water, regardless of origin. There are many ways in which water can become contaminated with oil.

When produced water is disposed into surface waters, the concentration of oil in the water is usually limited by government regulation.

- m. The *temperature* of the water affects the scaling tendency, the pH and the solubility of gases in water. The specific gravity of water is also a function of temperature.
- n. The *total dissolved solids* is simply the total amount of matter dissolved in a given volume of water. It can be calculated by taking the sum of the concentrations of all cations and anions shown on the water analysis report, or it can be measured by evaporating a sample of water to dryness and weighing the residue.
- o. *Specific Gravity*

$$\text{Specific Gravity} = \frac{\text{Density of Water Sample}}{\text{Density of Pure Water}} \quad (2.1)$$

Density is simply weight per unit volume. Pure water weighs 1 g/mL or 1000 kg/m³. Thus, a specific gravity greater than 1.0 means that the water sample of interest is more dense, or weighs more than an equal volume of pure water. Since the waters we are interested in contain dissolved solids, they are always more dense than pure water and therefore have a specific gravity greater than 1.0.

The magnitude of the specific gravity is a direct indicator of the total amount of solids dissolved in the water. Therefore, comparison of the specific gravity of several waters gives a rapid estimate of the relative amounts of solids dissolved in the waters.

A graph of total dissolved solids as a function of specific gravity is given in Appendix 6. This is an empirical correlation based on actual density measurements of oilfield waters.

Specific gravity is also a useful check on the accuracy of laboratory water analyses. If the quantity of dissolved solids calculated from the laboratory analysis drastically disagrees

with the amount estimated from the specific gravity correlation, there is a good chance that the analysis is in error.

- p. The **resistance** to electrical current flow is a function of the number of ions dissolved in the water. The lower the resistance the higher the concentration of ions dissolved in the water. It is a method of estimating total dissolved solids which is primarily applied to fresh, low TDS waters. Resistivity measurements are much more sensitive to small changes in TDS in fresh waters than specific gravity.

A chart showing the resistivities of sodium chloride solutions as a function of temperature is given in Appendix 7.

- q. **Conductivity** values are measured by some laboratories instead of resistivity. Conductivity is the reciprocal of resistivity and can be derived from resistivity values using the following formula:

$$\text{Conductivity } (\mu\text{mho} / \text{cm}) = \frac{1000}{\text{Resistivity } (\text{ohm} - \text{m})} \quad (2.2)$$

- r. **Silica** occurs in most well waters and can be a serious source of scale deposition in cooling waters and in steam boilers. It normally does not present any problems in water injection operations.

Water Analysis Techniques

Summary of Methods Used

Recommended techniques for measuring the concentration of the ions of interest are given in *API RP 45, Analysis of Oilfield Waters*.^(2,2) In addition, meters may be used to determine dissolved oxygen or pH; membrane filter analysis will be used to measure the suspended solids.^(2,3)

The types of techniques normally used to analyze an oilfield water sample are summarized in Table 2.3.

Chemical Quantitative Analysis

Quantitative analysis is simply the determination of how much of each of the individual constituents are present in a given sample. Three basic types of methods are commonly used to analyze water samples in the field. More sophisticated instrumental techniques may be used in an analytical laboratory.

Titration

An "indicator" is added to the water sample and a standard solution is then added drop-by-drop from a calibrated dispenser until the solution changes color. The point at which the solution changes color is called the **endpoint**. This simply means that you are finished titrating. The volume of standard solution used to reach the endpoint is noted and the amount of the unknown species present is calculated.

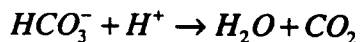
A titration is simply a method of determining the concentration of a particular substance in solution by reacting it with a known material. Reactions are used which are known to be complete at a given pH. A pH meter is normally used to detect the end point in the laboratory. However, color indicators (substances that change color at a specific pH value) are used for analyses carried out in the field.

TABLE 2.3
Summary of Analysis Methods

Determination	Analysis Method
Sodium	Calculation, spectroscopic, gravimetric
Calcium	Titration, gravimetric, spectroscopic
Magnesium	Titration, gravimetric, spectroscopic
Iron	Colorimetric, titration, spectroscopic
Barium	Turbidimetric, spectroscopic
Strontium	Spectroscopic
Chloride	Titration
Sulfate	Turbidimetric, gravimetric
Bicarbonate	Titration
Carbonate	Titration
pH	pH Meter, colorimetric, pH paper
Bacterial Population	Culturing, microscopic, others
Suspended Solids Concentration	Gravimetric
Particle Size	Coulter Counter, light scattering, microscopy
Particle Shape	Microscopy
Suspended Solids Composition	Chemical analyses
Turbidity	Turbidimetric
Water Quality	Membrane filter test
Dissolved Oxygen	Oxygen meter, titration, colorimetric
Carbon Dioxide	Titration
Total Sulfides	Alkasetzer test, colorimetric, titration
Oil-in-water	Colorimetric, spectroscopic, gravimetric
Temperature	Thermometer
Total Dissolved Solids	Calculation, gravimetric, conductivity
Specific Gravity	Hydrometer
Resistivity	Resistivity cell, calculation
Silica	Gravimetric, colorimetric, spectroscopic

The colors of some commonly used indicators are shown in Table 2.4 as a function of pH. The pH value at which the color change occurs is designated with a "T."

An example of a titration is the determination of bicarbonate ion (HCO_3^-) concentration by titration with HCl:



The reaction is complete at a pH of 4.5, so methyl orange is used as the indicator.

TABLE 2.4
Colors of Indicators

Colors of Indicators														
INDICATORS	<p>Increasingly Acid pH Neutral Increasingly Alkaline</p> <p>0 1 2 3 4 5 6 7 8 9 10 11 12 13 14</p>													
Litmus	Red						T	Blue						
Phenolphthalein	Colorless						T	Red						
Methyl Orange	Pink, Red						T	Orange						
Methyl Violet	Y, G, B						T	Violet						
Alizarin Yellow	Colorless						T	Yellow						

The concentration of the ion of interest is calculated based on the fact that one equivalent weight of the known, or standard solution, will react with one equivalent weight of the ion in the water sample.

$$E_{\text{standard}} = E_{\text{sample}}$$

Where: E_{standard} = number of equivalent weights of titrant (standard solution) added to water sample to reach end-point

E_{sample} = number of equivalent weights of ion of interest in water sample

By definition:

$$\text{Normality}(N) = \frac{\text{Number of Gram Equivalent Weights of Ion (E)}}{\text{Liters of Solution (L)}} \quad (2.3)$$

So:

$$[E = N \times L]_{\text{standard}} \quad \text{and} \quad [E = N \times L]_{\text{sample}}$$

Setting them equal to each other:

$$[N \times L]_{\text{standard}} = [N \times L]_{\text{sample}}$$

$$\left[N \times L \times \frac{1000\text{ml}}{L} \right]_{\text{standard}} = \left[N \times L \times \frac{1000\text{ml}}{L} \right]_{\text{sample}}$$

$$[N \times mL]_{\text{standard}} = [N \times mL]_{\text{sample}}$$

$$[N \times mL]_{\text{standard}} \times \left[\frac{1}{mL} \right]_{\text{sample}} = N_{\text{sample}}$$

The normality of the standard solution is known. The volume of the standard solution required to reach the endpoint and the volume of the water sample is measured. The equation can then be solved for the normality of the ion of interest in the water sample. Substituting:

$$\left[\frac{E}{L} \right]_{\text{sample}} = N_{\text{sample}}$$

$$[N \times mL]_{\text{standard}} \times \left[\frac{1}{mL} \right]_{\text{sample}} = \left[\frac{E}{L} \right]_{\text{sample}}$$

This enables us to calculate the number of equivalent weights of the ion of interest per liter of water. In order to determine the weight of the ion present in a liter, it is necessary to multiply both sides of the equation by the gram equivalent weight of the ion and convert grams to milligrams.

$$[N \times mL]_{\text{standard}} \times \left[\frac{1}{mL} \right]_{\text{sample}} \times EW(g) \times \frac{1000mg}{g} = \left[\frac{E}{L} \right]_{\text{sample}} \times EW(g) \times \frac{1000mg}{g}$$

All of this is the long way to arrive at the final formula which we use to calculate the results from a titration:

$$\frac{[N \times mL]_{\text{standard}} \times EW \text{ of ion} \times 1000}{mL \text{ of sample}} = \frac{mg}{L} \quad (2.4)$$

The API recommends the use of mg/L as the unit of concentration for water analyses. Therefore, it is suggested that all titration results be reported as mg/liter of the substance determined.

Sometimes ppm are used interchangeably with mg/L. This is correct only when the specific gravity of the water is very near 1.0, since:

$$mg/L = ppm \times S.G. \quad (2.5)$$

In most titrations certain ions other than the ion of interest will react with the standard solution. This can be a serious problem if the interfering ions are present in significant quantities relative to the amount of the ion of interest present. Table 2.5 lists some common titrations and the interferences for each.

TABLE 2.5
Common Titrations and Interferences^(2.2)

Ion	Titrant	Indicator	Interferences
CO ₃ ⁼	H ₂ SO ₄ or HCl	Phenolphthalein	Borate, silicate, sulfide and phosphate will be included in the values for carbonate and bicarbonate as are volatile fatty acid anions.
HCO ₃ ⁻	H ₂ SO ₄ or HCl	Methyl Purple or Methyl Orange	
Ca ⁺⁺	EDTA	Cal-Red, Calcon or Murexide	Barium and strontium are included with the calcium determination. Iron also interferes. Can be masked by triethanolamine when more than 20 mg/L is present.
Mg ⁺⁺	EDTA	Eriochrome Black T	
Cl ⁻	Silver Nitrate	Potassium Chromate (K ₂ CrO ₄)	Bromides, iodides, thiocyanates, phosphates, carbonates and sulfides precipitate silver ions. Iron, barium, lead, and bismuth precipitate chromate indicator.

Colorimetric Analysis

Colorimetric methods are widely used because of their simplicity. This type of test is based on addition of a material to the water sample which will react specifically with the species in question and produce a colored solution. The intensity of the color is proportional to the amount of the species present. The concentration of the substance in the water is found by comparing the color of the sample with the color standards of known concentration.

For example:



pH + various indicators → Spectrum of color

Battery-powered spectrophotometers or colorimeters are also available and can be used for many test procedures. The color-developing reagents are available in pre-weighed packets which are extremely convenient for field use.

One of the most convenient colorimetric analysis procedures employs an extremely clever unitized reagent and sampling system called a CHEMet® (CHEMetrics, Inc., Rt. 28, Calverton, VA 22016). Each CHEMet is a 7-mm diameter glass ampoule with a tapered, prescored tip. Color-forming reagents are sealed inside the ampoule under vacuum. When the user snaps the tapered tip of the ampoule in the sample, vacuum pulls the sample in automatically.

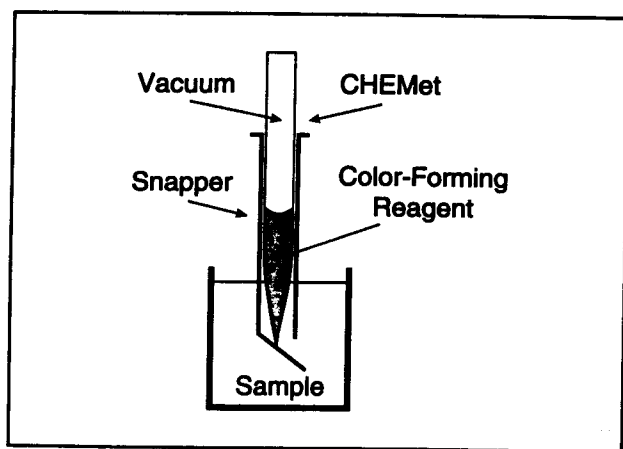


Figure 2.1 Using a CHEMet

Filling is instantaneous and complete except for a small bubble of inert gas. Sample and reagent are mixed by tilting the ampoule and allowing the bubble to travel from end to end several times. After waiting a specified period for color development (usually two minutes or less) the analyst quantifies the result using a color comparator supplied with the kit.

Although CHEMets are available for a fairly wide range of analyses, they have proven to be invaluable for the detection of low levels of dissolved oxygen. Test kits are available with ranges as low as 0-20 ppb (0-0.02 ppm). The results are expressed as mg/L O₂.

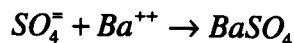
The results are not affected by temperature, salinity, other dissolved gases (including H₂S), or the presence of sulfite oxygen scavengers.

Oxidizing agents, such as chlorine, can cause high results unless a special formulation of the reagent is used.

Turbidimetric Analysis

In this type of analysis, a reagent is added to the water which will react with the ion of interest to form a finely divided precipitated solid. The precipitate creates a cloudy solution and the degree of cloudiness, or turbidity, is proportional to the amount of the ion present.

For example, turbidimetric analysis can be used to determine sulfate concentration.



Of the three analytical methods,

- Titration is the most accurate.
- Colorimetric techniques are the most sensitive (can detect the smallest quantities).
- Turbidimetric analyses are the least accurate.

Expression of Results

The concentration of different species in a water can be expressed in several different ways.

1. Milligrams per Liter (mg/L)

This is the unit of concentration recommended by the API for oilfield waters.

2. Milliequivalents per Liter (meq/L)

Some laboratories also report results in milliequivalents per liter.

$$meq/L = \frac{mg/L}{Equivalent\ weight} \quad (2.6)$$

3. Parts per Million (ppm)

If the water is very fresh, the specific gravity is essentially 1.0, and ppm and mg/L are equal. However, as the TDS of the water increases, the specific gravity increases and the units become increasingly different.

$$ppm = \frac{mg/L}{S.G.} \quad (2.7)$$

4. Equivalent per Million (epm)

This unit of concentration is calculated as follows:

$$epm = \frac{ppm}{Equivalent\ weight} \quad (2.8)$$

5. Grains/U.S. Gallon

Grains/gallon (gr/gal.) are units which are seldom used in routine oilfield water analysis work. However, they are used in calculations involving water softening by ion exchange.

$$gr/U.S.\ gal. = \frac{mg/L}{17.1} \quad (2.9)$$

6. ppm as CaCO₃

Watch out for this unit system as it is frequently used in cooling water and boiler water work. When the concentration of an ion is expressed in ppm as CaCO₃ this means that its concentration has been calculated using the equivalent weight of CaCO₃ (50) instead of the equivalent weight of the ion in question. This is done by multiplying the concentration of the ion by the ratio of the equivalent weight of CaCO₃ to the equivalent weight of the ion of interest.

For example:

$$\begin{aligned} \text{ppm } Ca^{++} \text{ as } CaCO_3 &= \text{ppm } Ca^{++} \times \frac{50}{20} \\ &= 2.5 \times \text{ppm } Ca^{++} \end{aligned} \quad (2.10)$$

In our work we are usually interested in just the reverse of the above procedure, i.e., converting results reported to us in ppm as $CaCO_3$ to ppm of the ion. Therefore, we do just the reverse of the above.

$$\begin{aligned} \text{ppm } Ca^{++} &= \text{ppm } Ca^{++} \text{ as } CaCO_3 \times \frac{20}{50} \\ &= 0.4 \times \text{ppm } Ca^{++} \text{ as } CaCO_3 \end{aligned} \quad (2.11)$$

A conversion table for converting ppm as $CaCO_3$ to ppm of the ion is given in Appendix 8.

Calcium carbonate equivalent concentration units are used in water softening calculations and is the standard method of expressing hardness and alkalinity.

7. Hypothetical Salt Combinations

Sometimes the reported results are expressed in ppm of hypothetical salts. The chemist may assume that all of the Ca^{++} present will be present as calcium bicarbonate, $Ca(HCO_3)_2$, for instance. This is not true, since the calcium is present in solution as the calcium ion, not as a salt. Many hypothetical combinations of ions are possible from a single ionic analysis. This unit system is not recommended.

8. Hardness

Total hardness is normally the sum of the calcium and magnesium concentrations expressed as equivalent $CaCO_3$.

$$(\text{ppm } Ca^{++} \times 2.5) + (\text{ppm } Mg^{++} \times 4.1) = \text{Total Hardness, ppm as } CaCO_3 \quad (2.12)$$

9. Alkalinity

Alkalinity in waters is usually attributed to the presence of bicarbonate, carbonate, and hydroxyl ions. However, each of these ions exists only in a given pH range. A general idea of the ions contributing to alkalinity as a function of the pH of the water is as follows:

TABLE 2.6
Ions Causing Alkalinity

pH	Ions Causing Alkalinity
9.6-14.0	OH^- and $CO_3^{=}$
8.3-9.6	HCO_3^- and $CO_3^{=}$
4.5-8.3	HCO_3^-

These relationships are not exact, and alkalinity is defined as the capacity of a water to react with hydrogen ions. The distribution of HCO_3^- and $CO_3^{=}$ ions as a function of pH is shown in Figure 3.1.

Alkalinity is determined by titrating with a standard acid to two different endpoints or pH values.

- **P Alkalinity:** A measure of the number of equivalents of acid required to lower the pH of the water to approximately 8.3 (the phenolphthalein, or "P" endpoint).
- **M Alkalinity:** A measure of the number of equivalents of acid required to lower the pH to approximately 4.5 (the methyl orange or "M" endpoint).

Most natural waters have a pH less than 8.3, and hence have a P alkalinity of zero and contain no CO_3^{2-} . This means that they show only M alkalinity, which is attributed solely to HCO_3^- .

Alkalinity and acidity as a function of pH is shown in Figure 2.2.

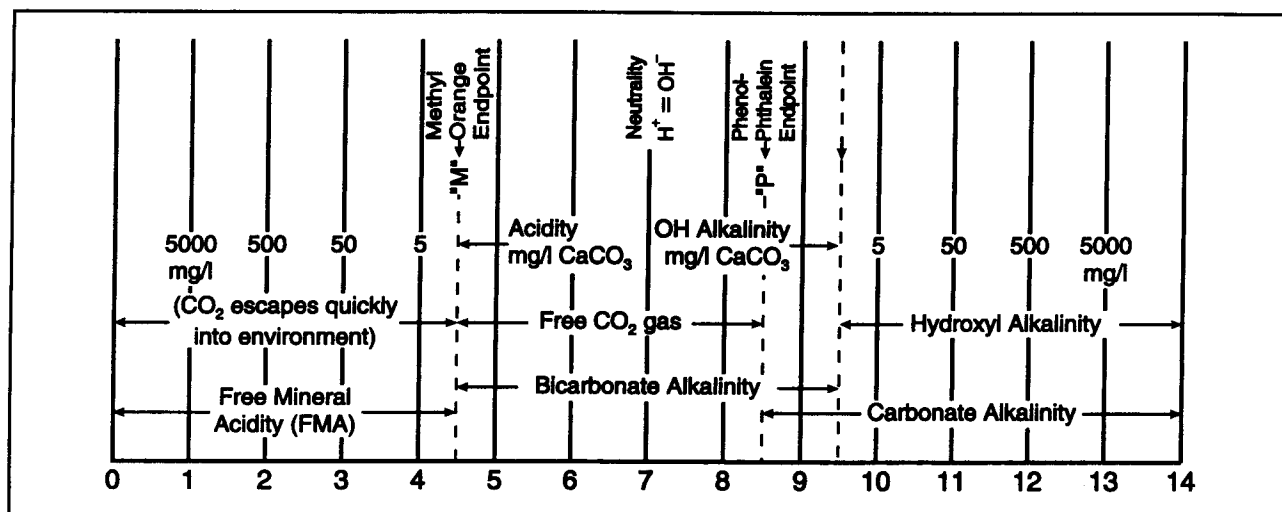
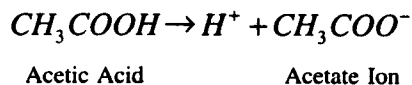


Figure 2.2 Alkalinity and Acidity Ranges

Although absent from surface waters and most aquifer waters, *carboxylic acids* are commonly present in produced waters (water produced with oil and/or gas) and are usually referred to as volatile fatty acids (VFA's). Even though they are classified as acids they are not actually present as acids in produced water because they have ionized to yield a hydrogen ion and a volatile fatty acid anion ("VFA anion").^(2,4) For example, in the case of acetic acid:



The VFA anions commonly found in produced water contribute to alkalinity and are listed in Table 2.7.

TABLE 2.7
Volatile Fatty Acid Anions

VFA Anions	Formula
Acetate Ion	CH_3COO^-
Propionate Ion	$\text{CH}_3\text{CH}_2\text{COO}^-$
Butyrate Ion	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$

Alkalinity in produced waters is the sum of the concentrations of the bicarbonate ion and the VFA anions.

$$\text{Alkalinity} = \text{HCO}_3^- + \text{Acetate} + \text{Propionate} + \text{Butyrate} \quad (2.13)$$

The acetate ion usually comprises the major portion of the VFA anions in produced waters with considerably smaller quantities of propionate and even smaller concentrations of butyrate ions.

The concentration of the VFA anions in produced water can be substantial relative to the bicarbonate concentration. When this occurs, the bicarbonate ion concentration determined by titration with acid will be significantly in error.

Accurate determination of the HCO_3^- concentration in these types of waters requires the measurement of the VFA anion concentration so that it can be subtracted from the total alkalinity. This measurement is not routinely performed and must be requested if desired. This can be quite important when making calcium carbonate scaling calculations.

Graphical Presentation of Results — Water Patterns

Water analyses are often expressed graphically. The diagram, or pattern, obtained by graphically plotting the results of a water analysis will often highlight important points about the analysis that might be missed by simply reading the report. Pattern comparison is also an easy way to quickly spot differences in two or more waters.

There are many different water analysis diagrams in use. However, the Stiff Method^(2.5) has been adopted by the API and is probably the most universally used method in the oilfield. It is the only one presented here. A logarithmic plot of meq/liter of the various ions is most often used, although linear plots are also used. The concentrations of Na^+ , Ca^{++} , Mg^{++} , Fe (total), Cl^- , HCO_3^- , $\text{SO}_4^{=}$ and $\text{CO}_3^{=}$ given in Table 2.8 are plotted as shown in Figure 2.3.

TABLE 2.8
Water Analysis

Ion	mg/L	meq/L
Na^+	93230	4053
Ca^{++}	5173	258
Mg^{++}	620	51
Fe (Total)	12	0.6
Cl^-	153175	4320
HCO_3^-	195	3
$\text{SO}_4^{=}$	1910	40
$\text{CO}_3^{=}$	0	0

The concentrations of the cations are plotted to the left of the center line, while the anion concentrations are plotted to the right of the center line.

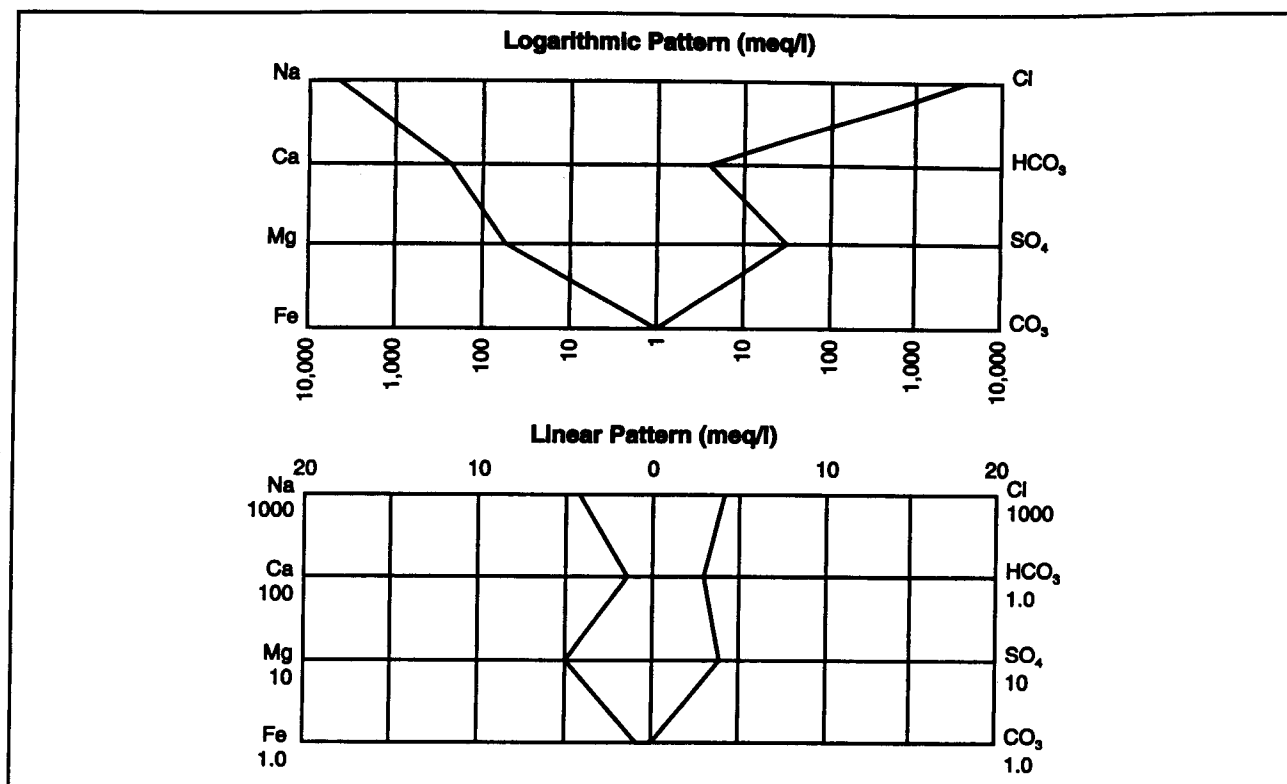


Figure 2.3 Graphical Presentation of Water Analysis — Stiff Method

Water Analysis Reports

Appendix 9 contains examples of two water analysis reports. The first is presented on a modified API Water Analysis Report form. The second report presents the same data in a slightly different format used by a commercial water analysis laboratory.

Both reports contain the following:

- Sample identification information.
- Quantitative analysis of water sample. The degree of detail will vary.
- A graphical representation of the analysis — a water pattern.

The Stiff Method is used in both cases, although the logarithmic pattern is used in the first form while the linear pattern is used in the second.

The API report form is recommended for your own field analysis work. You may find it desirable to eventually modify the form to contain space for reporting additional information pertinent to your own operation.

Oil-in-Water Analysis

The oil content of a water depends on how it is measured. There is no absolute value.

Produced water contains both dispersed oil and “dissolved oil”. The dissolved oil consists of hydrocarbons, phenols, organic acids, and low molecular weight aromatic compounds such as benzene and toluene.

Normal oil/water separation equipment cannot remove dissolved organic compounds. However, values of "oil and grease" include *both* the dispersed oil and dissolved organic compounds. Hence, equipment performance should not be judged by "oil and grease" values.

Oil and Grease

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, the amount of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in freon. Oil and grease may include hydrocarbons, fatty acids, soaps, fats, waxes, oils, and any other material that is extracted by the solvent from an acidified sample unless it evaporates during the test procedure. Oil and grease is defined by the method used for its determination.

Gravimetric: EPA Method 413.1

The water sample is acidified to a low pH (< 2). The acidified water sample is then poured into a glass container along with freon (fluorocarbon-113) and shaken vigorously. Any oil and grease present is extracted from the water into the freon. The freon is then evaporated from the extract at 70°C , and the residue (oil and grease) is weighed. The results obtained include both dispersed oil and dissolved organic compounds. Any hydrocarbons which will evaporate at this temperature are lost.

Infrared: EPA Method 413.2

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then placed in an infrared spectrophotometer and the infrared absorption is measured at a wavelength of 2930 cm^{-1} . This wavelength is characteristic of the carbon-hydrogen bond. The oil and grease content of the sample is obtained by comparing the measured value with standards prepared using the same oil. The results obtained include both dispersed oil and dissolved organic compounds.

Results obtained by this method are usually considered to be a more accurate reflection of the true oil and grease content of the water than gravimetric results since the sample is not heated and the loss of light ends is minimized.^(2,6)

Petroleum Hydrocarbons

Petroleum Hydrocarbons: EPA Method 502 E

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then mixed with silica gel. Water soluble polar organic materials are removed from the freon by adsorption on the silica gel. Petroleum hydrocarbons remain in the freon and can be determined by either the gravimetric or infrared methods.

Oil Content by Colorimetric Analysis

The water sample is *not* acidified. Oil is extracted from a water sample using a dense solvent such as trichloroethane. The color intensity of the extract is compared with standards prepared with the same oil to determine the concentration.

This is a very useful field technique and is commonly used to assess equipment performance; however, the sensitivity of the method is limited with light colored oils such as condensates.

Suspended Solids Analysis

Techniques for suspended solids determination and characterization are not covered in API RP 45.^(2.2) Because of the extreme importance of suspended solids control in water handling operations, a brief summary of techniques used to determine the amount and nature of suspended solids in a water is presented in the following sections.

Suspended Solids Concentration

The concentration of suspended solids in a water is determined by passing a known quantity of water through a membrane filter and determining the weight of solids collected on the filter. The weight of solids collected (mg) divided by the quantity of water passed through the filter (liters) gives the suspended solids concentration in mg/L. Standard methods for this test are given in NACE Standard TM0173-92 published by the National Association of Corrosion Engineers.^(2.7)

It is strongly recommended that water be flowed *directly from the system* through the membrane, when possible, as shown in Figure 2.4. This approach eliminates problems of secondary precipitation associated with sample aging and contact with atmospheric oxygen.

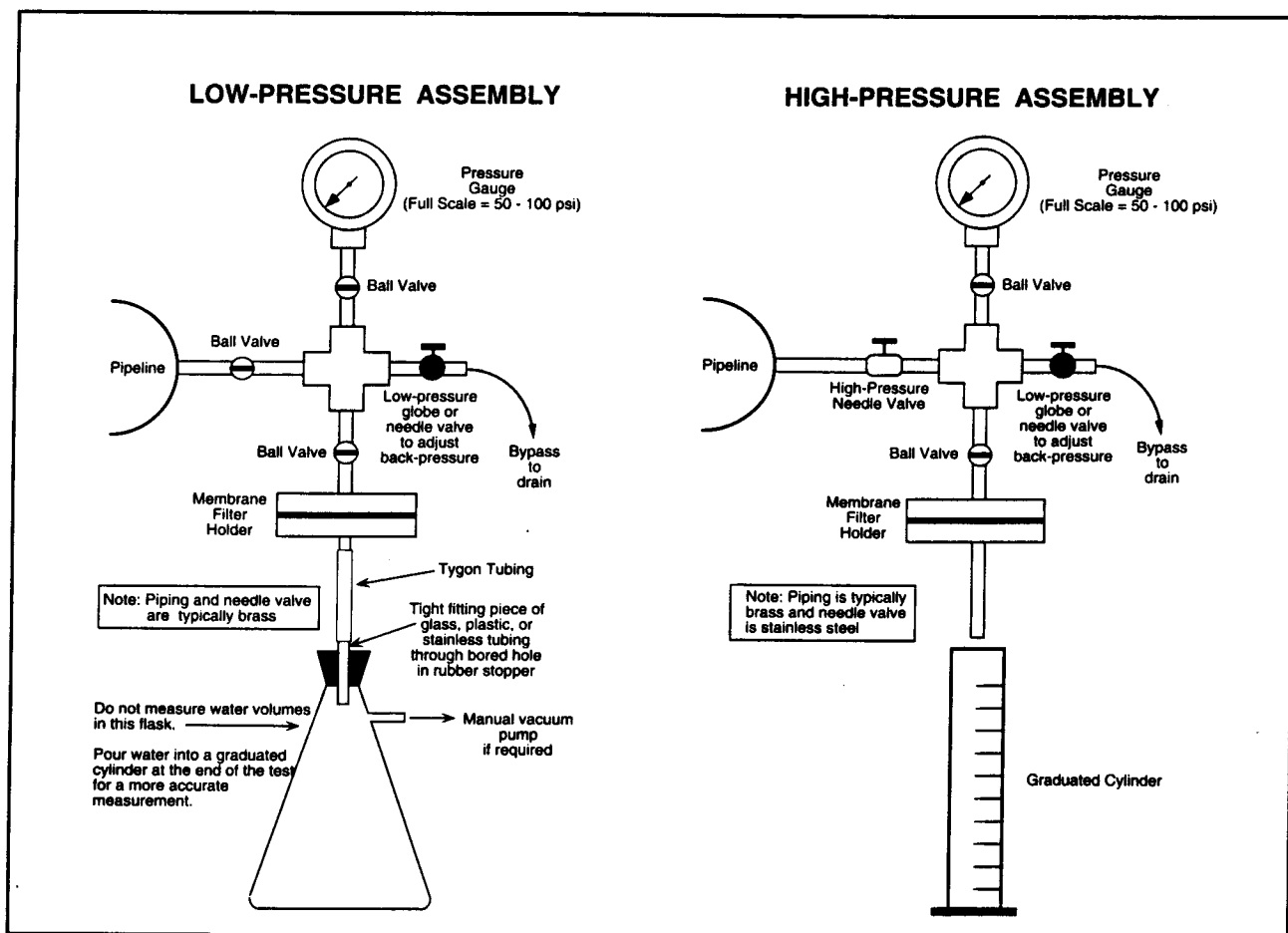


Figure 2.4 Membrane Filter Test Apparatus

Suspended solids are sometimes collected by flowing a water sample from the system into a clear plastic cylinder which has been purged with nitrogen or some other inert gas. Water is then displaced from the cylinder through a 0.45 μm membrane filter by applying approximately 20 psi pressure to the

cylinder with a nitrogen bottle. This method is often used at low-pressure sample points although it is sometimes used at high-pressure sample points as well.

The use of a pressurized plastic cylinder may give acceptable results in some waters but it is not recommended for general use. It is particularly unreliable for produced waters. The basic problem arises from the fact that a large volume of water is transferred from the system into the plastic cylinder (typically several liters) but only a small portion of the water (often a few hundred milliliters in poor quality waters) passes through the membrane filter before it plugs and flow ceases. Two things typically occur:

1. Oil tends to rise to the surface of the water and to coat the walls of the plastic cylinder. The net result is that the amount of oil passing through the membrane filter is less than occurs when the sample is drawn directly from the system. This effects the permeability of the filter cake and hence the volume of water which will flow through the cake at a given pressure drop.
2. Suspended solids tend to segregate in the cylinder, with the larger particles settling to the bottom. This gives a non-representative sample.

Although this technique is widely used, and is indeed a NACE-recommended *alternate* method, we strongly recommend that suspended solids be collected directly from the system using an apparatus such as one of those shown in Figure 2.4.

The most common reason for using the pressurized cylinder method is that system pressure becomes irrelevant. Furthermore, the pressure drop across the membrane filter is always the same, which is very handy when water quality testing (flow rate vs. cumulative volume at a constant ΔP) is performed. A pressure drop of 20 psi is typically chosen because it is the value recommended by NACE for water quality testing.

However, the pressure drop across the membrane filter is not important when the sole purpose is to determine the suspended solids concentration in the water. If the pressure at the sample point is low, the pressure drop across the membrane filter can be increased by using a hand-operated vacuum pump as shown in Figure 2.4.

The test is normally conducted using a single pre-weighed membrane filter when the suspended solids content is 1 mg/L or greater. When the concentration is less than 1.0 mg/L, matched weight membranes or pre-weighed pairs are preferred.

It is critical that the increase in weight of the membrane filter due to solids filtered from the water be sufficient to provide analytical accuracy. For example, a 47-mm diameter, 0.45 μm pore size, membrane filter weighs about 100 mg. At least 2 mg of solids should be filtered from the water so that the weight gain will be at least 2%. This means that the suspended solids concentration determines the amount of water which must be filtered to provide the minimum weight gain required.

Elution Loss

There is one complicating factor when large quantities of water are passed through the standard cellulose acetate/cellulose nitrate membrane filter: the water dissolves a small amount of the filter, resulting in a small loss of weight. This weight loss is referred to as *elution loss*. This loss is not significant when the amount of solids collected on the filter is large. However, elution loss can be quite significant in waters containing low levels of suspended solids.

It has been common practice to deal with this problem by running matched-weight filters. Filtration through two matched-weight membrane filters mounted in series subjects both filters to the same

elution loss but all solids are collected on the top filter. Therefore, the differential weight is the suspended solids corrected for elution loss.

However, it is not necessary that the two filters be matched in weight. If both are pre-weighed, the elution loss correction can be determined from the bottom filter and applied to the top filter.

Another option is to use a different membrane material, such as polyvinylidene difluoride (PVDF) which is not subject to elution loss.

Chemical Composition of Suspended Solids

An analysis procedure for the determination of solids composition is given in TM0173-92.^(2.7) Determination of hydrocarbon solubles, acid solubles, organics and insoluble residue should be supplemented by chemical analyses to identify the major components of each fraction. Of specific interest is iron, sulfate and carbonate, supplemented by determinations of calcium, barium, and strontium as deemed necessary. Analysis for silica and protein may also be of interest.

When membrane filters are used in brines, the membrane must first be washed with deionized water prior to weighing and analysis. The purpose of the wash is to remove water-soluble salts which precipitated in the filter when the water evaporated from the wet membrane during drying. They are not a part of the suspended solids.

A typical analysis format for suspended solids is shown in Table 2.9.

TABLE 2.9
Analysis of Suspended Solids

Component	mg/L	mg/L
Total Acid Solubles		1.50
Calcium as CaCO ₃	0.13	
Iron as FeS	0.40	
Unidentified	0.97	
Total Organics		3.55
Solvent Soluble (Oil)	1.70	
Ignition Loss	1.85	
Total Acid Insolubles		0
Total Suspended Solids		5.05

Water Quality

In water injection systems, water quality is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of 0.45 μ m is most commonly used.

The National Association of Corrosion Engineers has approved a standard method for running the test.^(2.7) Several modified methods are used. However, the basic test consists of forcing a given volume of water through a filter under constant pressure. The cumulative volume through the filter is recorded as a function of time, and the flow rate for each time increment is calculated from the data. Flow rate is plotted versus cumulative volume throughput on a semi-log plot. The slope of the line indicates the "quality," or degree of plugging which occurred with that particular water sample, as illustrated in Figure 2.5.

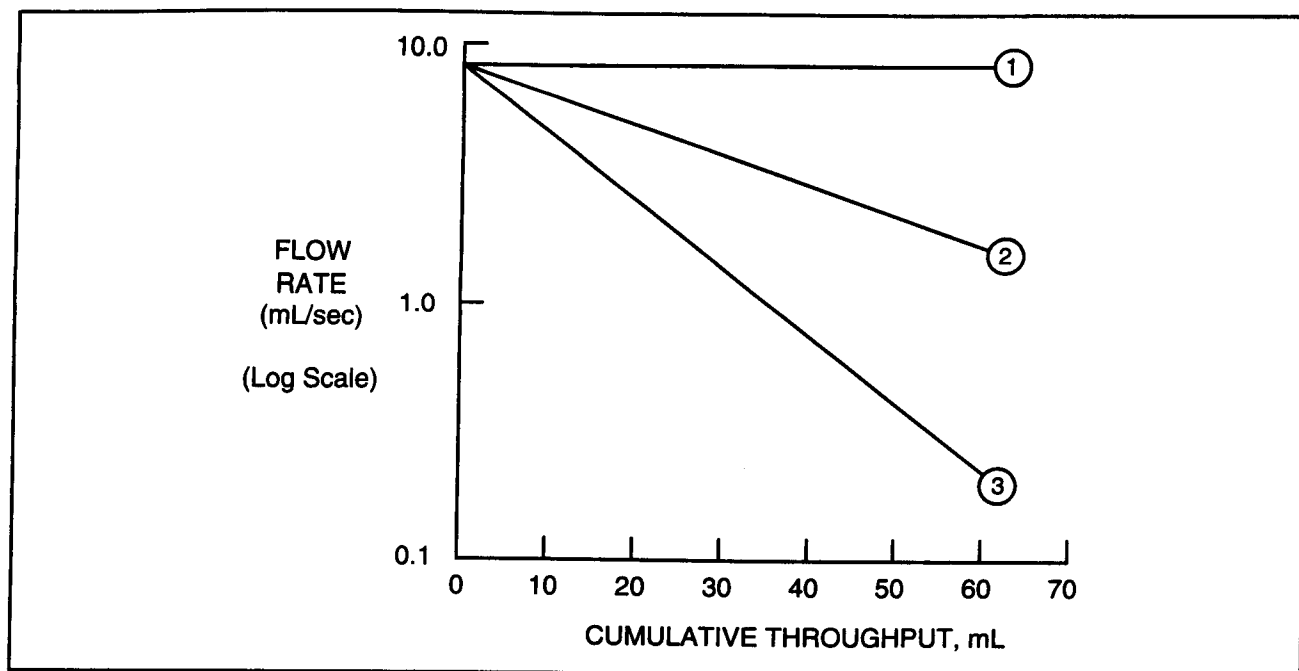


Figure 2.5 Water Quality Plot

It is also a measure of the permeability of the filter cake formed on the membrane. The steeper the slope, the less permeable the cake formed by the solids.

The important point to be made about water quality testing is that it is a way of comparing the relative tendency of different waters to plug a membrane filter. It does not necessarily have any correlation with the tendency of a water to plug the formation.

TABLE 2.10
Interpretation of Water Quality Curves in Figure 2.5

Curve	Quality
1	Excellent. No plugging occurred since the flow rate remained constant throughout the test.
2	Poorer than Curve 1. The flow rate decreased as the cumulative volume throughput increased indicating plugging of the filter.
3	Poorest of the three curves. The flow rate dropped much more rapidly indicating faster plugging.

The utility of water quality testing lies largely in its use as a comparative test.

- Water quality testing can be used to detect changes in a single water at a given point in a system over a period of time.
- Tests can be run at various points through a system to detect changes which may be occurring between the water source and the injection wells.
- Different waters can be compared.
- Through experience, minimum water quality standards may be set for a specific area. Careful correlation of water quality measurements with injectivity data can be very helpful in determining filtration requirements.

Any insoluble material in a water will reduce its quality. Corrosion products, water-formed scales, clay, silt, oil, insoluble treating chemicals, bacterial growths or algae will all contribute to decreased quality.

It should be obvious that the quality required will be largely determined by the reservoir permeability. Tight, low permeability zones will require better water than a high permeability reservoir. What is considered acceptable quality in one area (or zone) might quickly plug a different formation.

Cerini Slope Measurements

In 1953, William F. Cerini proposed a novel means of measuring the slope of water quality curves.^(2.8) Although he used a sintered glass disc rather than membrane filters for his test work, his slope measurement technique is still widely used in water-quality work.

The water quality data is plotted in the normal way on two cycle semi-log graph paper. A best fit straight line is drawn through the points, and the slope is then measured as though it were a linear Cartesian plot.

Both the vertical and horizontal components of the slope are measured using the same linear scale. The slope value is then calculated by dividing the vertical component (y) by the horizontal distance (x). As long as the curve slopes downward to the right, the slope value is always negative, and is commonly called the Cerini Slope.

The Cerini Slope of the curve shown in Figure 2.6 is $-2.4/1.5 = -1.6$.

Cerini Slope values are a function of scales used on both the ordinate and the abscissa. Therefore, slope values can be compared only when the scales are fixed.

Relative Plugging Index

Amoco developed a method of rating water quality called the Relative Plugging Index, or RPI.^(2.9)

$$RPI = TSS - MTSN \quad (2.14)$$

Where: TSS = Total suspended solids, ppm
 MTSN = Millipore test slope number

Millipore Test Slope Number (MTSN)

The MTSN is the Cerini Slope of a conventional water quality curve, with fixed ordinate and abscissa scales:

Vertical "y" axis (Ordinate): 1 cycle/5 inches

Horizontal "x" axis (Abscissa): 500 mL/inch

The MTSN is determined as follows:

1. Plot the water quality data, log flow rate (mL/sec) vs cumulative volume (mL), on 2-cycle semi-log graph paper.
2. Draw a best fit straight line through the data points in the latter portion of the curve as illustrated in Figure 2.6.
3. Select two points on the curve. The coordinates of the selected points are designated as (Q_a, V_a) and (Q_b, V_b) .
4. Calculate MTSN directly from the data or determine it graphically.

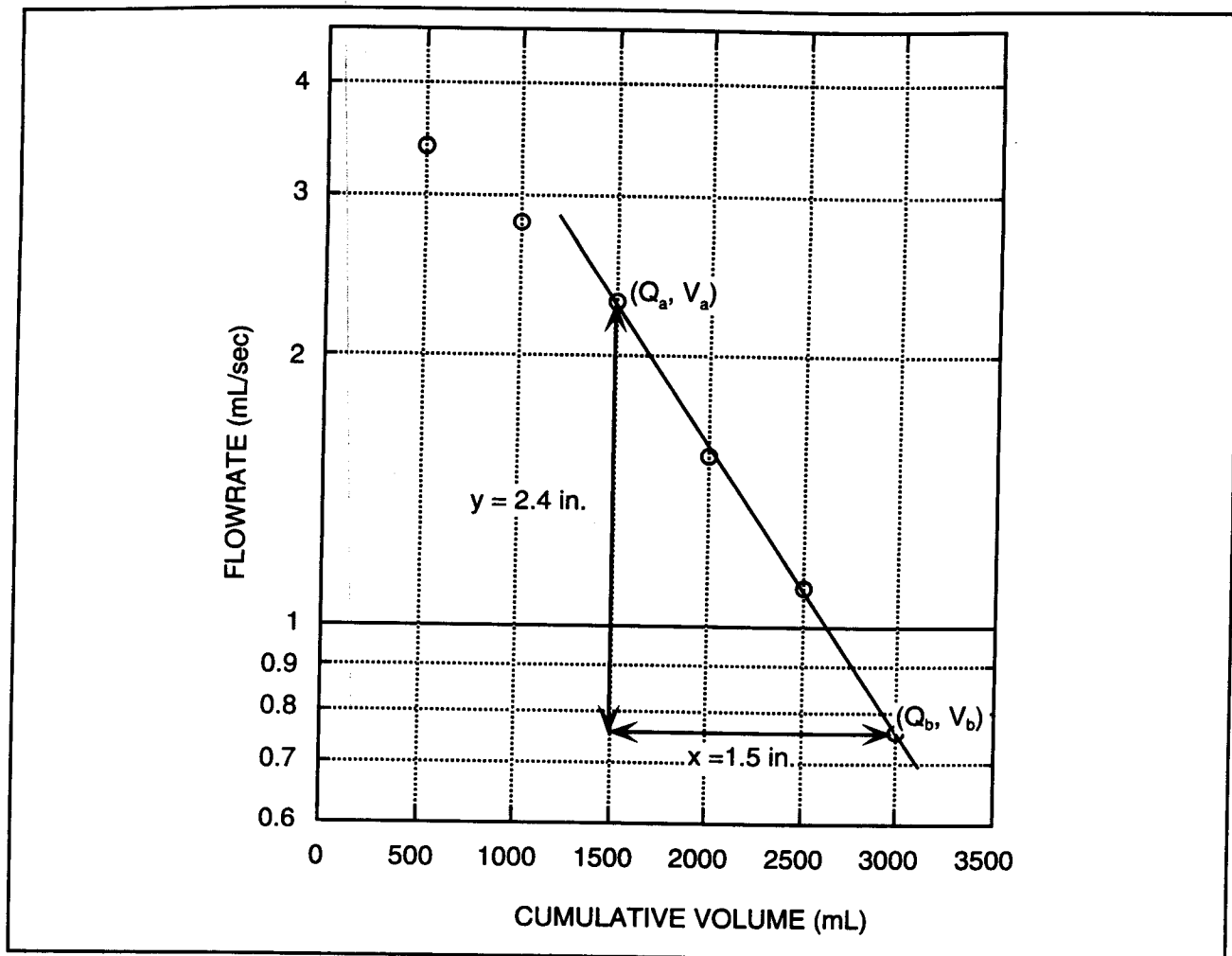


Figure 2.6 Measurement of Cerini Slope

The simplest way to determine the MTSN is to calculate it using the following equation:

$$MTSN = \frac{2500 \log(Q_a/Q_b)}{V_a - V_b} \quad (2.15)$$

Use of this equation permits you to use any ordinate and abscissa scales you choose.

If you wish to determine the MTSN graphically, it is necessary to use graph paper with an ordinate scale of 1 cycle/5 inches, which is usually quite convenient, since that is the normal grid size on 2-cycle semi-log graph paper (8-1/2 × 11 sheet).

There are two options regarding the abscissa scale:

1. Use an abscissa scale of 500 mL/inch.
2. Use an abscissa scale other than 500 mL/inch and calculate the equivalent distance on a 500 mL/inch scale using the following formula:

$$x \text{ (inches)} = \frac{V_a - V_b}{500 \text{ mL/inch}} \quad (2.16)$$

MTSN is determined graphically as follows:

1. Measure the vertical distance between Q_a and Q_b , y .
2. Measure the horizontal distance between V_a and V_b , x . If the scale on the horizontal axis is other than 500 mL/in., calculate the difference between the two volumes in milliliters, and divide by 500 to obtain the correct value of x in inches.
3. $MTSN = \frac{-y}{x}$ The MTSN is always negative.

Example 2.1: Given the water quality data in Table 2.11:

The data is plotted in Figure 2.6. The MTSN of the water quality curve is calculated as follows:

$$MTSN = \frac{2500 \times \log(2.3/0.76)}{1500 - 3000} = \frac{2500 \times 0.48}{1500} = -0.8$$

The MTSN can also be determined graphically:

1. $y = 2.4$ inches
2. $x = \frac{3000\text{mL} - 1500\text{mL}}{500\text{ mL/inch}} = 3.0$ inches
3. $MTSN = \frac{-y}{x} = \frac{-2.4}{3.0} = -0.8$

TABLE 2.11
Water Quality Data

Flow Rate (mL/sec)	Cumulative Volume (mL)
3.40	500
2.90	1000
2.30	1500
1.55	2000
1.10	2500
0.76	3000

Water Quality Rating Guide

A water quality rating guide proposed by Amoco is given in Table 2.12.^(2.9)

Well Impairment Prediction

Another approach to the presentation and interpretation of water quality data was developed by Barkman and Davidson.^(2.10) They developed methods and theory which can be used to interpret water quality data obtained with membrane filters or cores to predict well impairment from suspended solids.

Although this method can be used to make relative predictions, the calculated half-life values have proven to be unreliable in practice.

TABLE 2.12
Water Quality Rating Guide

RPI	General Quality Rating
< 3	Excellent
3-10	Good to Fair
10-15	Questionable
> 15	Poor

Particle Size Analysis

Solid particles found in injection waters range in diameter from less than one micron up to several hundred microns. Figure 2.7 shows the diameters of some commonly encountered particles for comparison.

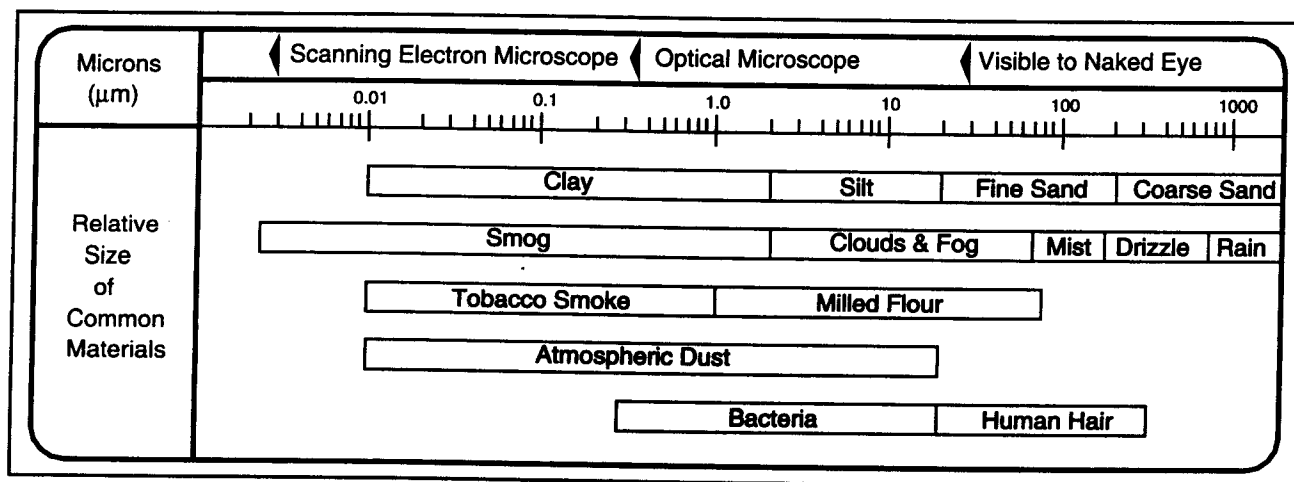


Figure 2.7 Typical Diameter of Common Particles

Although many of the particles found in injection waters are approximately spherical, many are not.

The description of the "size" of a non-spherical particle is one of the fundamental problems of particle technology. The most common approach is to describe the particle by a sphere which will have at least one property in common with it. Thus, a single particle may have several "equivalent sphere sizes" depending on the method used for its measurement, as shown in Table 2.13.








Note that for the particle shown the "diameter" varies by more than a factor of two among the various measurement techniques.

There are a number of techniques which are used to determine the size of particles suspended in water. They are compared in Table 2.14 and discussed in the following paragraphs.

Microscopic Techniques

The use of visual microscopy is probably the oldest technique used to examine particles in oilfield waters. However, it is a rather tedious way to measure particle size distributions, as many particles must be examined if the distribution determined is to be statistically valid. It is more generally used to determine the shape and nature of the particles and to get some idea of their general size range.

TABLE 2.13
Diameters Used for Particle Characterization^(2.11)

<u>METHOD OF MEASUREMENT</u>	<u>KIND OF "DIAMETER" MEASURED</u>	<u>EQUIVALENT SPHERES</u>	<u>DIAMETER VALUE ANY UNITS</u>
	True Particle		$d \times h \times w = 1 \times 1 \times 2$
Microscope	Projected-Area Diameter		$d_p = 1.58$
Microscope	Maximum Feret ^a Dia.		$d_f = 2.23$
Sedimentation	Stokes Diameter ^b		$d_{st} = 1.43$
Coulter Counter	Volume Diameter		$d_v = 1.55$
Sieve	Mesh-Size Diameter		$d = 1.00$
HIAC Counter	Surface-Area Diameter		$d = 1.77$
^a Maximum distance between parallel tangents. ^b Stokes diameter is included in the expression $3\pi\eta d$, which is the force (resistance to motion) exerted on a particle.			

Scanning electron microscopy (SEM) is a popular method of particle examination. Much higher magnifications are possible than with conventional microscopy, and the depth of field is far superior.

Figure 2.8 is an SEM photograph of suspended solids filtered from Aegean seawater, while Figure 2.9 is an SEM photo of solids filtered from North Sea Water.

Both waters contained virtually identical concentrations of suspended solids, but the shapes and types of particles were quite different.

Coulter Counter

Two electrodes are immersed in a beaker of the water of interest, which must contain sufficient dissolved ions to easily conduct electrical current.

The negative electrode is located inside a glass tube which is sealed except for a tiny hole or orifice on the side of the tube. The positive electrode is located in the water sample beaker. (Figure 2.10)

A constant electrical current is passed from the positive electrode to the negative electrode through the orifice. When a non-conductive particle passes through the orifice it causes a change in electrical resistance between the two electrodes which is proportional to the volume of the particle.

TABLE 2.14
Comparison of Commonly Used Particle Analysis Techniques

Technique	Approx Size Range	Sample Requirements	Data Produced	Instrument Portability	Maximum Magnification
Visible Light Microscope		Usually filtered solids on surface of membrane filter although drops of water can be examined.	Particle shape and size.	Easily portable. Requires AC power for illuminating lamp.	800 x (Dry objective) 1500 x (Oil immersion)
Scanning Electron Microscope		Filtered solids on surface of membrane filter. Must be plated with Au or Pd prior to examination. Sample examined under vacuum.	Particle shape and size.	Permanent laboratory installation.	100 000 x
Coulter Counter	0.5 μm to 400 μm	Representative water sample. Counts particles in liquid. Water must have sufficient TDS to be electrically conductive.	Particle size distribution or total number greater than a manually set threshold.	Portable. Requires AC power.	
Spectrex Particle Counter	1 μm to 100 μm	Representative water sample. Counts particles in liquid.	Total number of particles greater than a manually set threshold.	Portable. Requires AC power.	
HIAC and Royco Counters	2 μm to 900 μm	Flowing water sample piped through flow cell or batch sample.	Particle size distribution	Portable. Most require AC power. Some battery powered units available.	

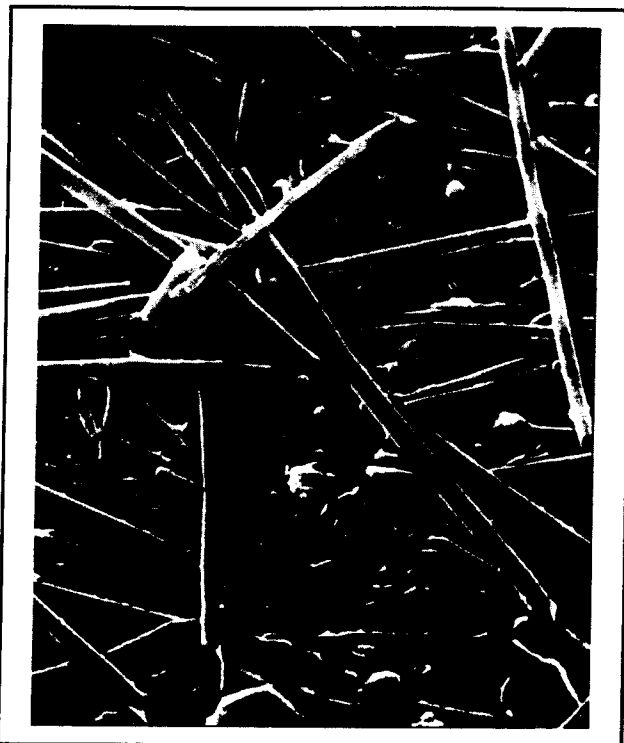


Figure 2.8 Suspended Solids Filtered from Aegean Seawater
Magnification = 1000 x
(Courtesy Brown & Root, Inc.)

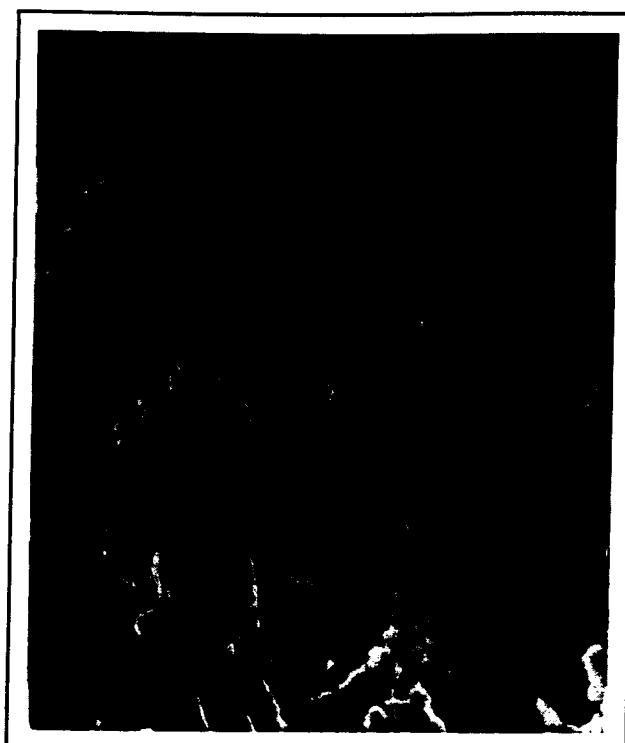


Figure 2.9 Suspended Solids Filtered from North Sea Water
Magnification = 1000x
(Courtesy Nalffloc Ltd.)

A fixed volume of water containing suspended particles is forced through the orifice. As each particle passes through the orifice, the increased resistance results in a voltage pulse which is proportional to particle volume. The series of pulses produced by a series of particles passing through the orifice are electronically scaled and counted, yielding a particle size distribution.

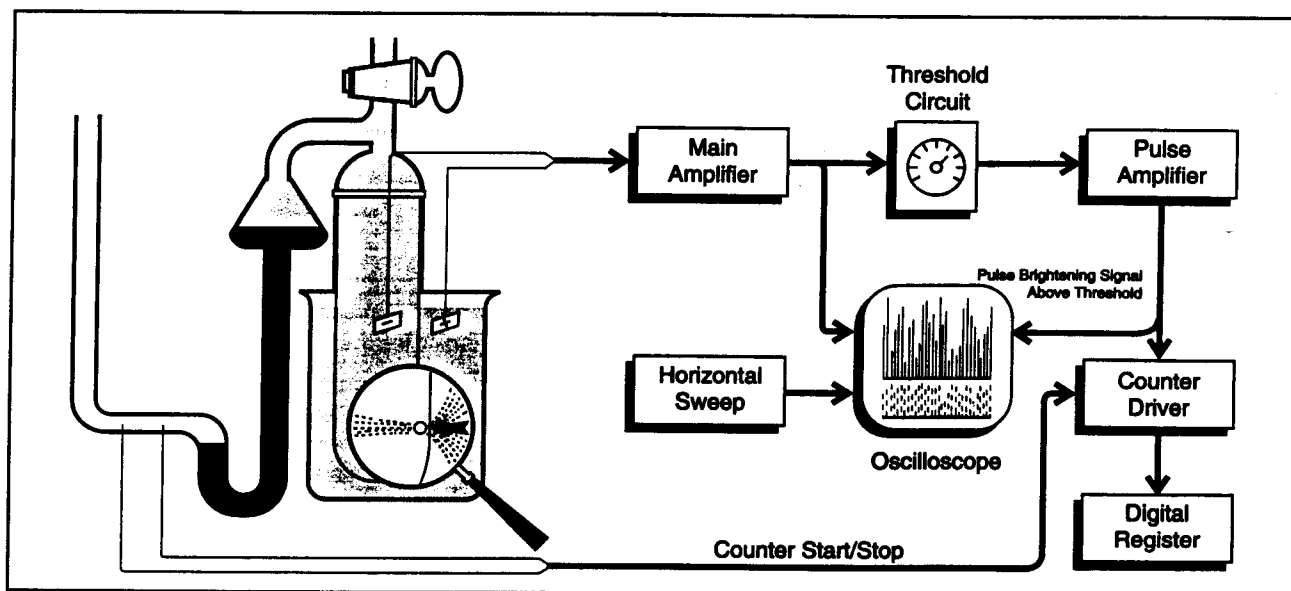


Figure 2.10 Coulter Counter Schematic (Courtesy Coulter Electronics Ltd.)

It must be realized that the particle "diameter" given by the counter is the diameter of a fictitious sphere with the same **volume** as the real particle. Thus, the more non-spherical the particle, the greater the error.

It should be noted that the Coulter Counter cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Light Scattering Counters

Instruments such as those manufactured by HIAC (HIAC Instruments Div., Pacific Scientific Co., Montclair, California) and Royco (Royco Instruments, Inc., Menlo Park, California) use the principle of light absorption/total scatter, or light blockage, to detect particles in a fluid. Water is flowed through a sensor cell and as each particle passes through the intense beam of light in the sensor, it scatters the light. The instrument measures the magnitude of each pulse of scattered light which is proportional to the **surface area** of the particle. The particle diameter given by the instrument is the diameter of a sphere with the same surface area as the particle.

The Spectrex Laser Particle Counter (Spectrex Corp., Redwood City, California) operates on the same principle, but uses a laser as a light source. Furthermore, in this instrument, the water sample remains stationary while the laser scans the sample. A sample container of water is placed in the instrument and the laser is activated. The beam revolves rapidly as shown in Figure 2.11, thus scanning a fixed volume of the sample. It gives a count of the total number of particles per milliliter above a certain manually set threshold between 1 μm and 100 μm .

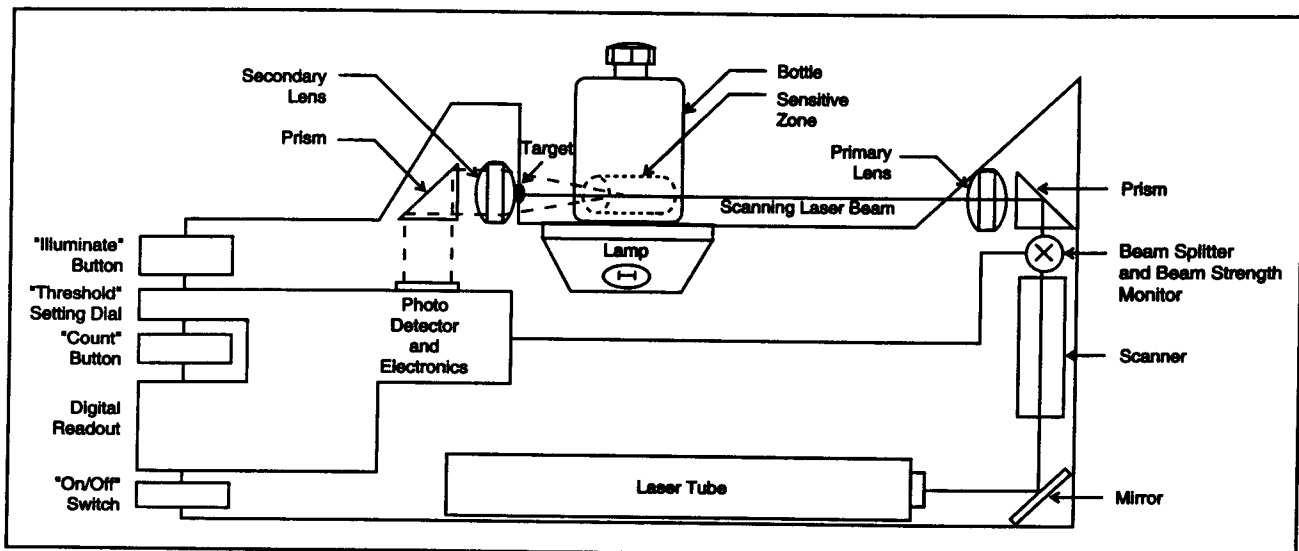


Figure 2.11 Spectrex Particle Counter (Courtesy Spectrex)

As in the case of the Coulter Counter, light-scattering particle counters cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Membrane Filter Analysis

Membrane filters **should not be used** to estimate the size of suspended solid particles in water, as the results have little meaning.

Two techniques are used.

1. Filter a water through two membrane filters in series, the second filter having a smaller pore size than the first, and measure the amount of suspended solids on each filter. The assumption is that the results can be used to estimate the concentration of particles in different size ranges.

For example, filter one liter of water through a 5 μm pore-size filter followed by a 2 μm pore-size filter as shown in Figure 2.12. Determine the weight of suspended solids on each filter.

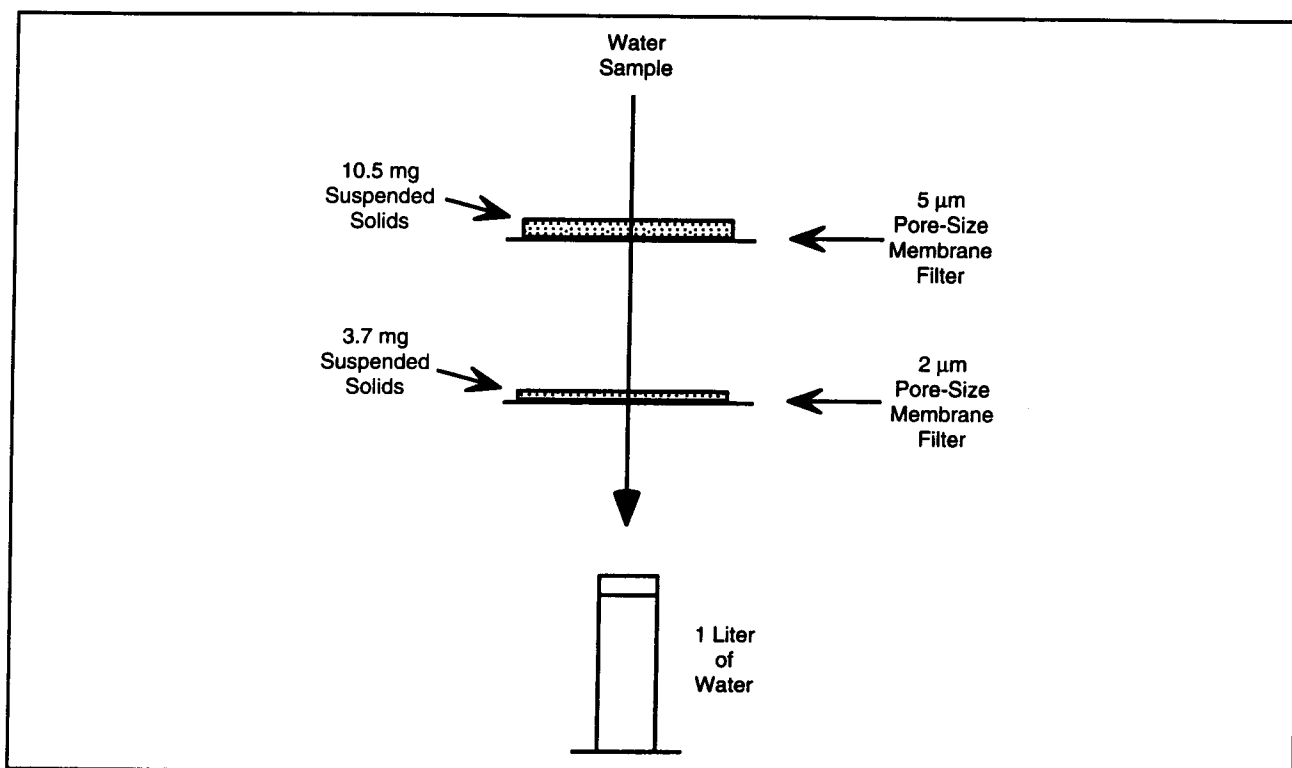


Figure 2.12 Filtration Through Membrane Filters in Series to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu\text{m}$	10.5 mg/L
$5\mu\text{m} > D > 2\mu\text{m}$	3.7 mg/L

This concept is analogous to a sieve analysis for sizing dry particles. However, the set of sieves is shaken vigorously throughout the sieving operation which prevents bridging and gives each particle in the sample the opportunity to pass through a given mesh-size.

Particle bridging occurs when particles are filtered from a liquid slurry which often results in the removal of particles smaller than the membrane pore size. The filter cake formed on the membrane becomes the filter.

2. The second technique employed is to filter a given water through a membrane of a given pore size. Then a second sample is filtered through a different pore size. Consider the example shown in Figure 2.13.

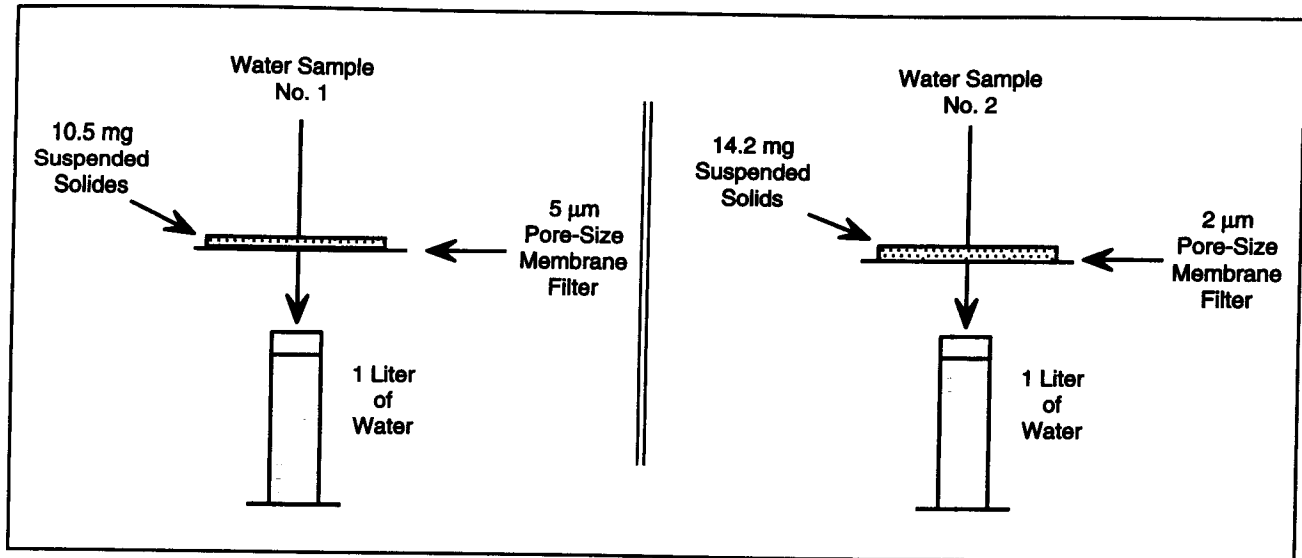


Figure 2.13 Filtration Through Membrane Filters in Parallel to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu m$	10.5 mg/L
$5\mu m > D > 2\mu m$	$14.2 - 10.5 = 3.7$ mg/L

Once again, the assumption is made that all particles with diameters less than the pore-size of the membrane filter being used will pass through the filter. However, this is not true because of particle bridging.

Filtration of particles from a liquid slurry is a process which is distinctly different from a sieve analysis of dry particles and *should never be used* to estimate particle sizes.

Turbidity

Turbidity is an optical property of a liquid which is related to the ability of undissolved particles to scatter light.

In most cases we are interested in a correlation between turbidity and suspended solids content. Unfortunately, *no general correlation is possible* because turbidity values are dependent upon the size, color, shape and refractive index of the particles, as well as the refractive index of the carrier medium. It is also dependent upon the wavelength of the incident light and the orientation of the scattered light detector, which means that different types of instruments can give different readings. A correlation between turbidity and suspended solids concentration can be made for a specific water containing a given quantity and size distribution of suspended particles. However, since turbidity values are a function of particle size, a change in particle size distribution will alter the measured turbidity.

Figure 2.14 illustrates the relationship between particle size and the amount of scattered light for a constant weight concentration of suspended particles. The optical response may be divided into three zones:

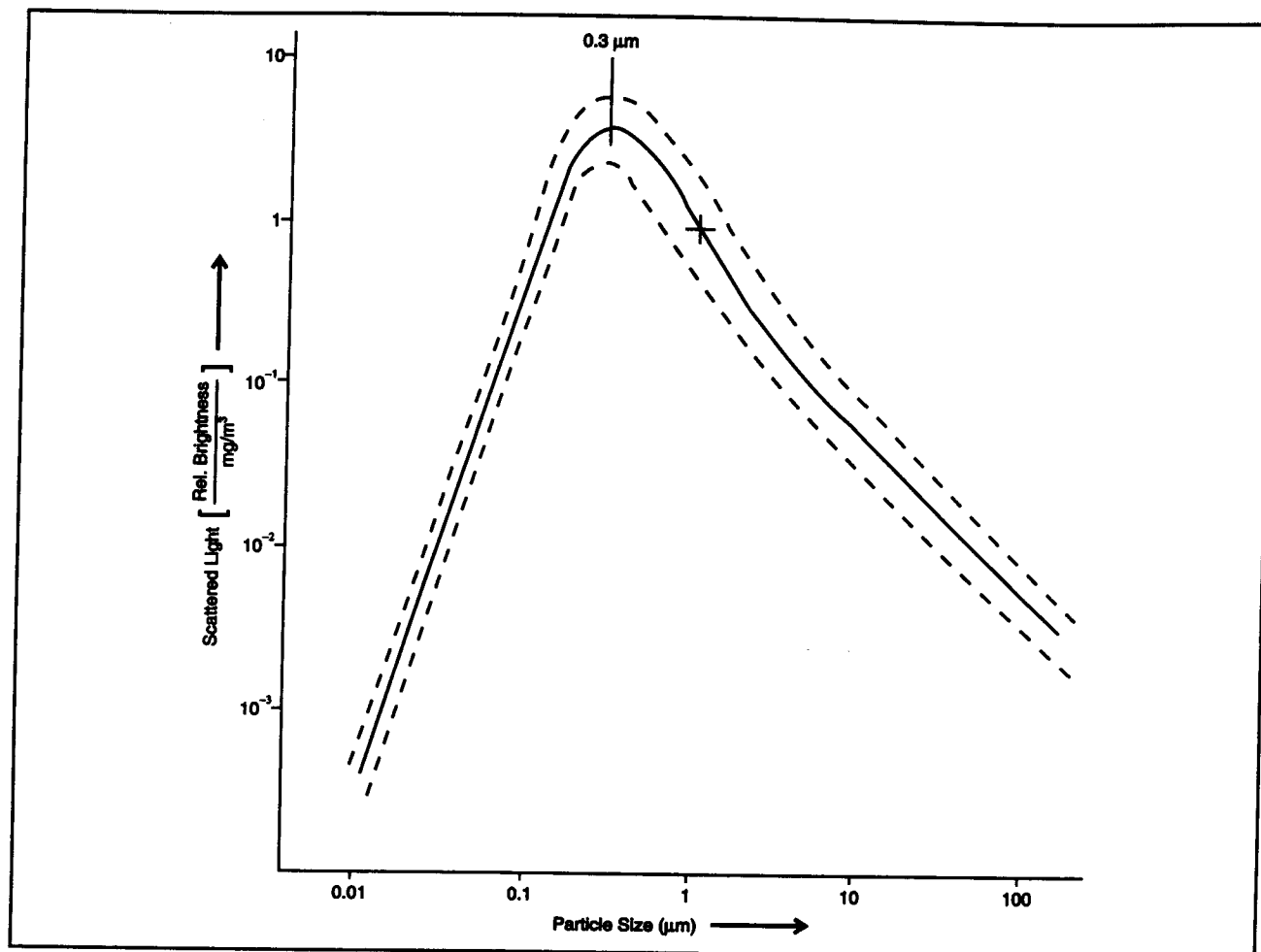


Figure 2.14 Scattered Light as a Function of Particle Size (Courtesy Sigris-Photometer AG)

TABLE 2.15
Scattered Light vs Particle Size

Particle Size	Amount of Scattered Light
<0.1μm	Increases with particle size
0.1μm-1.0μm	Complex transition zone
>1.0μm	Proportional to total surface area. Decreases with particle size

Remember that these relationships apply when the concentration of suspended solids remains constant and only particle size changes. Above 1.0 μm, for example, the amount of light scattered is greater for a larger particle because it is proportional to surface area. However, as particle size increases, it takes fewer particles to give the same weight of suspended solids. The net result is a decrease in the total amount of light scattered.

When a ray of light hits a particle it is scattered in all directions. However, it is not scattered uniformly in all directions, with the result that the scattered light reading obtained for a given particle will be a function of the position of the detector.

For particles less than $0.1\ \mu\text{m}$ diameter, the forward and backscattered intensities are equal, with half that intensity in the perpendicular direction (side scatter) as shown in Figure 2.15.

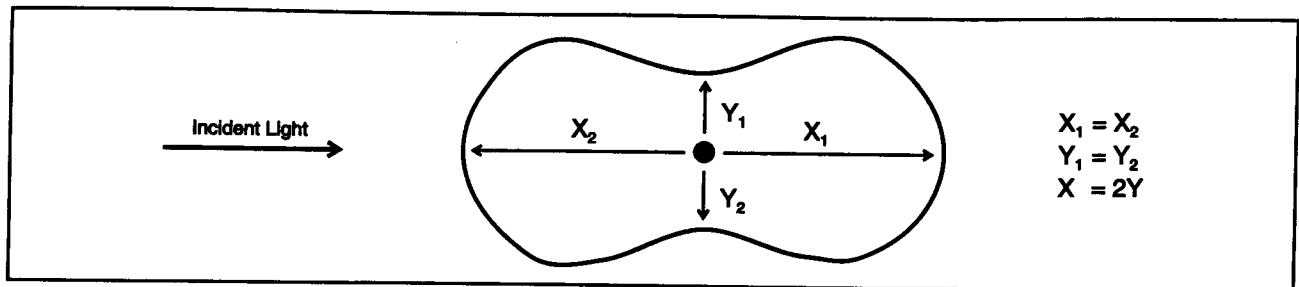


Figure 2.15 Angular Distribution of Scatter Light (Particle Diameter $< 0.1\ \mu\text{m}$)

The pattern is not affected by particle shape as long as no dimension of the particle is greater than $0.1\ \mu\text{m}$.

For particles larger than $0.1\ \mu\text{m}$, the amount of forward scatter increases relative to the amount of back and side-scatter (Figure 2.16).

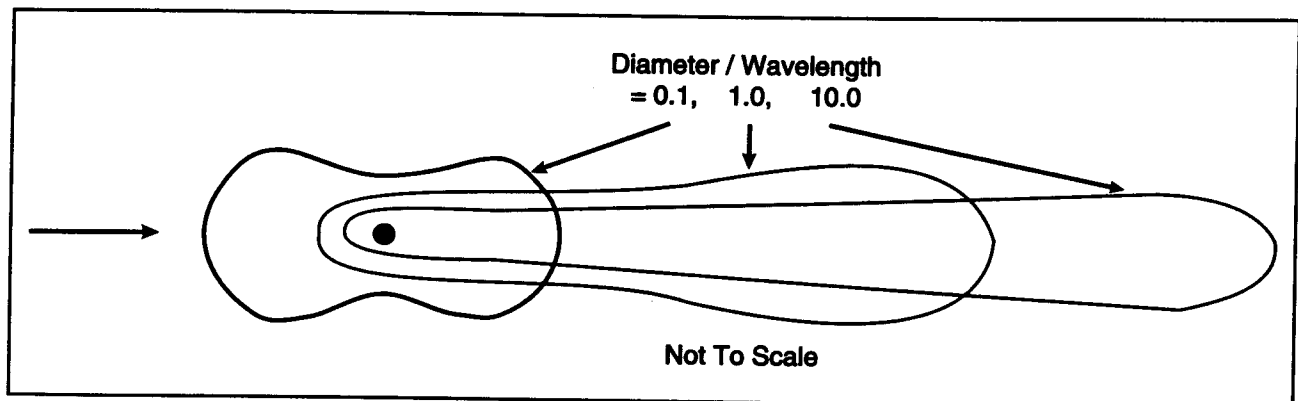


Figure 2.16 Angular Distribution of Scattered Light for Different Particle Diameters
(Courtesy Monitor Technology, Inc.)

The shape and orientation of non-spherical particles will modify the pattern, but in practical situations, the random orientation of the particles will generate essentially the same results as spherical particles of the same average volume.

There are many turbidity instruments on the market. The majority used in water injection systems either measure side scatter or forward scatter. An instrument which measures side scattered light at an angle of 90° to the incident light is called a nephelometer. Forward scatter instruments usually measure the scattered light at an angle of $15\text{--}30^\circ$ to the incident light beam.

Selection of an instrument for a particular water should be based on a knowledge of the nature and size distribution of the suspended particles, and a careful investigation of the response characteristics of each instrument being considered.

The units in which turbidity measurements are reported can be extremely confusing.

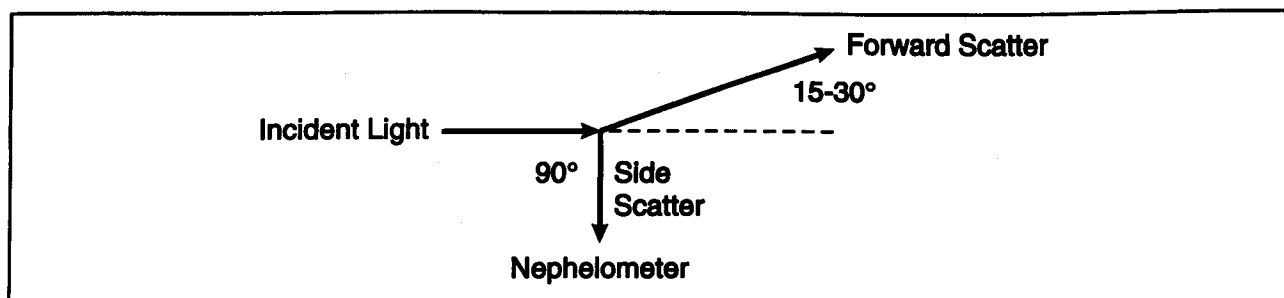


Figure 2.17 Scattered Light Direction

The father of modern turbidimeters is the Jackson Candle Turbidimeter. It consists of a vertical glass tube, graduated in units of length, and a candle as shown in Figure 2.18.

A sample of liquid is poured into the tube until the candle can no longer be clearly seen. The height of liquid at which this occurs is dependent upon its turbidity. A standard table is used to convert this height into Jackson Candle Units (JCU's), also called Jackson Turbidity Units (JTU's). With the advent of modern turbidimeters, other units began to appear. These units are based on calibrations made with standard suspensions of materials such as kieselguhr (diatomaceous earth or SiO_2), fullers earth, or formazin (a polymer suspension). Of the many units in use, the following are the most common:

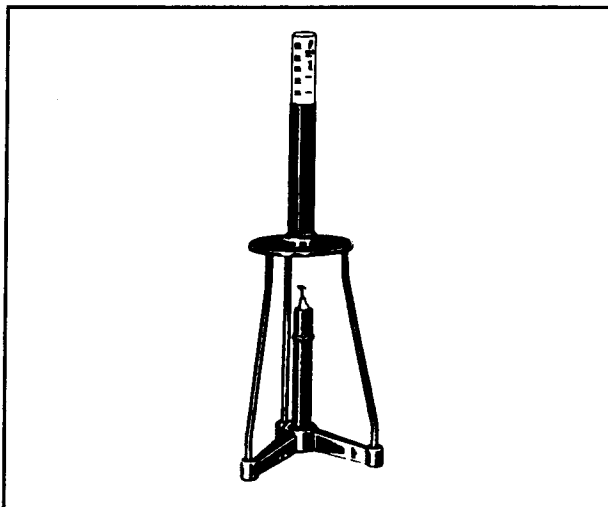


Figure 2.18 Jackson Candle Turbidimeter

- **FTU** — Formazin turbidity unit. An instrument is calibrated in FTU's with a standard suspension of formazin. Unfortunately, at least three different "standard" suspensions are used, resulting in three different formazin units.
- **NTU** — Nephelometer turbidity units are used solely for nephelometers. Nephelometers can be calibrated with kieselguhr, fullers earth or formazin.
- **PPM** — Parts per million. Actually ppm of the calibration suspension, which usually is diatomaceous earth (SiO_2) or fullers earth. It's use was originally intended to detect breakthrough of DE particles downstream of DE filters. It is not the concentration of the suspended solids in the water.

To make matters more confusing, readings taken with a particular instrument in a given water may not agree with readings taken with another type of instrument in the same water, even when the same turbidity units are being used. This can result from differences in calibration techniques, instrument design or the angle at which the scattered light sensor is located. Conversion among different unit systems must be made with extreme caution.

In summary, turbidimeters are extremely valuable instruments for monitoring suspended solids levels in water systems. However, a separate correlation between suspended solids concentration and turbidity values must be made for each water using a specific turbidity measuring instrument.

Field Water Analyses

As previously stated, certain water properties change very quickly after sampling. The determinations listed in Table 2.16 must be made on-site for maximum accuracy:

- The suspended solids should be collected in the field with a membrane filter by allowing a stream of water to flow through the filter. The filter paper and the collected solids are normally taken to a laboratory for analysis.
- Particle size distribution carried out with either a Coulter Counter or a light scattering device must be performed on a fresh sample to minimize the effect of precipitation of solids after sampling.
- The culture media should be inoculated in the field immediately after sampling, if possible. (See Chapter 5)

TABLE 2.16
On-Site Measurements

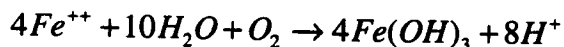
Parameters to be Measured On-Site	
pH	Temperature
Carbonate Ion	Suspended Solids Concentration ^(2.1)
Bicarbonate Ion	Particle Size Distribution ^(2.2)
Dissolved Oxygen	Turbidity
Dissolved Carbon Dioxide	Water Quality
Total Sulfides as H ₂ S	Bacteria Counts ^(2.3)

It is difficult to overemphasize the importance of field analyses. Certain properties may begin to change within minutes; others will be stable for several hours; and some are stable indefinitely.

For example, the pH and dissolved gas content of produced water will usually begin to rise immediately after the sample is taken. This results from the fact that dissolved acid gases begin to escape from solution as soon as the sample is removed from the system due to the reduction in pressure.

The rise in pH along with an increase in temperature may result in the formation of calcium carbonate scale. Bacteria in the sample may begin to multiply within a few hours — or they may begin to die — depending on specific conditions. Little or no H₂S or CO₂ may be found in the sample after a short time period.

If the sample contains dissolved iron, exposure to atmospheric oxygen will result in the precipitation of the iron due to reaction with oxygen.



The generation of hydrogen ions will cause the pH of the sample to drop and lead to an error in the measured value. This is yet another reason why the pH should be measured on-site in a flowing sample.

Thus, if the sample were transported to a laboratory and analyzed after several days, the resulting analyses would give a very distorted picture of the water as it actually existed in the system, because of the changes in water composition which took place after the sample was removed from the system.

Had it been a sample of fresh surface water or a sample of seawater, different changes would be anticipated. However, regardless of the water source, field analyses are absolutely necessary for an accurate and meaningful assessment of oilfield water problems.

Field water analysis kits are available from several manufacturers, as are oxygen analysis equipment, pH meters, and membrane filter equipment. This equipment, and someone skilled in its use, is required during initial sampling, for monitoring of system performance, and for trouble shooting. If you or someone in your organization do not have field analysis skills, then reliable outside personnel should be retained to do the work for you. The important point is that on-site measurement of certain water properties is an integral part of the successful design and operation of a water injection system. Make certain that this point is not overlooked, and that the measurements are carried out by experienced personnel.

General Instructions for Making Analytical Determinations in the Field

Cleanliness

The axiom that "cleanliness is next to Godliness" is the first rule of life to an analytical chemist. Although we may occasionally get a bit sloppy in performing analyses in the field, it is important that we follow this rule as closely as possible in our own analytical work.

The laboratory analyst uses glass beakers, flasks and burettes which he carefully washes and cleans between each usage. This mode of operation is very unhandy in the field. Experience has shown that the use of plastic beakers (disposable), disposable plastic or glass syringes, plastic bottles (disposable) and glass bottles where necessary (disposable) is much easier. Our motto is "Never use anything twice." Throw it away rather than risk contaminating the sample.

The reasoning behind this preoccupation with cleanliness is extremely sound. If you go to a great deal of time and trouble to obtain an uncontaminated, representative water sample and then use a dirty beaker or burette to run your analysis, you have just wasted a lot of time. Your sample is contaminated by any material which may have remained in the analytical ware from the previous analysis. It may or may not have ruined your present analysis, but the chances are good that it has. There are many sources of uncertainty under the best of circumstances. Do not use dirty lab ware and avoid at least one of the known sources of error.

It is permissible to re-use some of the disposable beakers or syringes when analyzing a given water sample. Between determinations they should be carefully rinsed with de-ionized water or preferably with some of the water sample of interest. They must be thrown away after completing the analysis of the sample.

Some discretion is required in the question of cleanliness. If you want to take the time and trouble to clean up your plastic beakers and syringes between determinations, you can do so, just as is done with glassware in a laboratory. However, it is simply often very inconvenient or impossible to do so in the field. The use of inexpensive, disposable materials gives you the alternative of starting with new, clean materials each time. This procedure offers the dual advantage of saving you time and trouble, and of minimizing the possibility of contamination.

Use of Syringes

Syringes are very handy for measuring water sample volumes in the field instead of burettes. A sample volume of 10 mL or 25 mL is most common.

Syringes can also be used for titrating instead of a burette. One-mL and 5-mL syringes are most common for this purpose.

You should always use at least one-half of the volume of any syringe, whether you are measuring a sample or titrating. With less than half of a syringe volume, you lose accuracy. Use a smaller syringe instead.

Normally, when measuring a water sample volume, a needle is not used with the syringe. Titrations are made with syringes equipped with needles so that the titrant may be dispensed drop-by-drop. The use of syringes is detailed in Appendix 10.

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WATER FORMED SCALES

Solubility is defined as the limiting amount of a solute which can be dissolved in a solvent under a given set of physical conditions. The chemical species of interest to us are present in an aqueous solution as ions. Certain combinations of these ions are compounds which have very little solubility in water. The water has a limited capacity for maintaining these compounds in solution, and once this capacity, or solubility, is exceeded the compounds precipitate from solution as solids. Therefore, precipitation of solid materials which may form scale can occur if *both* of the following conditions are satisfied:

1. The water contains ions which are capable of forming compounds of limited solubility.
2. There is a change in physical conditions or water composition which lowers the solubility below the concentrations present.

Solid precipitates may either stay in suspension in the water, or they may form a coherent scale on a surface such as a pipe wall. Formation plugging may occur by filtration of suspended particles from the water. Or, a solid scale may form on the formation face. Either is undesirable. The difficulty of removal varies with the type of plugging which has occurred.

Scale formation frequently restricts flow through injection and flow lines, and tubing strings. It causes pump wear or plugging and creates additional rod loads when it forms on sucker rods. Fire tubes in all types of heaters fail prematurely when scale formation results in overheating. Corrosion is often more severe under a scale deposit.

Water formed scales are responsible for many production problems and their effective control should be one of the primary objectives of any efficient water handling operation.

COMMON SCALES

Of the many possible water formed scales, only a few are commonly found in oilfield waters. These scales are listed in Table 3.1 along with the primary variables which affect their solubility.

Calcium Carbonate

Calcium carbonate scale can be formed by the combination of calcium ion with either carbonate or bicarbonate ions as follows:



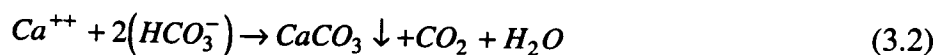


TABLE 3.1
Common Oilfield Scales

Name	Chemical Formula	Primary Variables
Calcium Carbonate (Calcite)	CaCO ₃	Partial pressure of CO ₂ , pH, temperature, total pressure, total dissolved solids.
Calcium Sulfate Gypsum (Most Common) Hemi-Hydrate Anhydrite	CaSO ₄ • 2 H ₂ O CaSO ₄ • 1/2 H ₂ O CaSO ₄	Temperature, total dissolved solids, pressure.
Barium Sulfate	BaSO ₄	Temperature, total dissolved solids, pressure.
Strontium Sulfate	SrSO ₄	Temperature, total dissolved solids, pressure.
Iron Compounds Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferric Hydroxide Ferric Oxide	FeCO ₃ FeS Fe(OH) ₂ Fe(OH) ₃ Fe ₂ O ₃	Dissolved gases, corrosion. Temperature, pressure, pH

Effect of CO₂ Partial Pressure

The presence of CO₂ increases the solubility of CaCO₃ in water. When carbon dioxide dissolves in water, it forms carbonic acid, which ionizes according to the following series of equations:



Only a small percentage of the bicarbonate ions dissociate at the pH values found in most injection waters to form H⁺ and CO₃⁼, as shown in Figure 3.1. Bicarbonate ions vastly outnumber the number of carbonate ions present under normal circumstances. Therefore, it is thought that Equation 3.2 is the more accurate expression for the precipitation of calcium carbonate.^(3.1)

As the concentration of CO₂ in solution is increased, the reaction shifts to the left, resulting in less CaCO₃ precipitation. The water also becomes more acidic (the pH decreases) with the addition of CO₂ to the water.

The amount of CO₂ that will dissolve in water is proportional to the partial pressure of CO₂ in the gas in contact with the water:

$$\text{Partial Pressure of } CO_2 = (\text{Mole Fraction of } CO_2 \text{ in Gas}) \times (\text{Total Pressure}) \quad (3.6)$$

$$\text{Mole Fraction of } CO_2 = \%CO_2 \text{ in Gas} + 100 \quad (3.7)$$

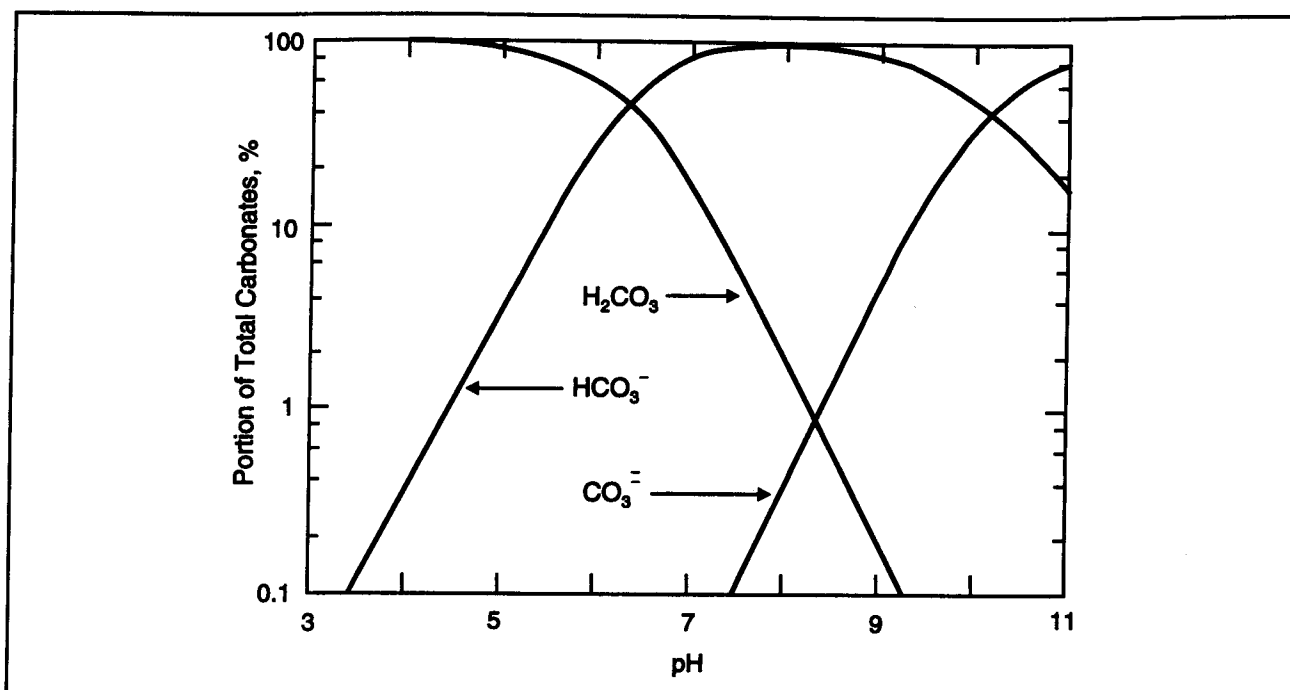


Figure 3.1 Ionization of Carbonic Acid as a Function of pH

Hence, if a two-phase (gas + water) system is operating at 100 psia [690 kPa] and the associated gas contains 10 mol % CO₂ (1 mole of CO₂ per 10 moles of gas), the partial pressure of CO₂ in the gas is:

$$(0.1)(100) = 10 \text{ psia [69 kPa]}$$

So, if either the system pressure or the percentage of CO₂ in the gas were to increase, the amount of CO₂ dissolved in the water also would increase.

Figure 3.2 illustrates the effect of CO₂ partial pressure on the pH of water containing little or no dissolved minerals. This data should not be applied to brines since the presence of dissolved minerals changes the relationship between pH and the amount of dissolved CO₂.

The effect of CO₂ pressure on the solubility of CaCO₃ in pure water is shown in Figure 3.3.

This data illustrates that CaCO₃ solubility increases with increased CO₂ partial pressures. The effect becomes less pronounced as the temperature increases.

The reverse is also true. It is one of the major causes of CaCO₃ scale deposition. At any point in the system where a pressure drop is taken, the partial pressure of CO₂ in the gas phase decreases, CO₂ comes out of solution, and the pH of the water rises. This shifts Reaction 3.2 to the right and may cause CaCO₃ precipitation.

Effect of pH

The amount of CO₂ present in the water affects the water pH and the solubility of calcium carbonate. However, it really does not matter what causes the acidity or alkalinity of the water. The higher the pH, the more likely that precipitation will occur.

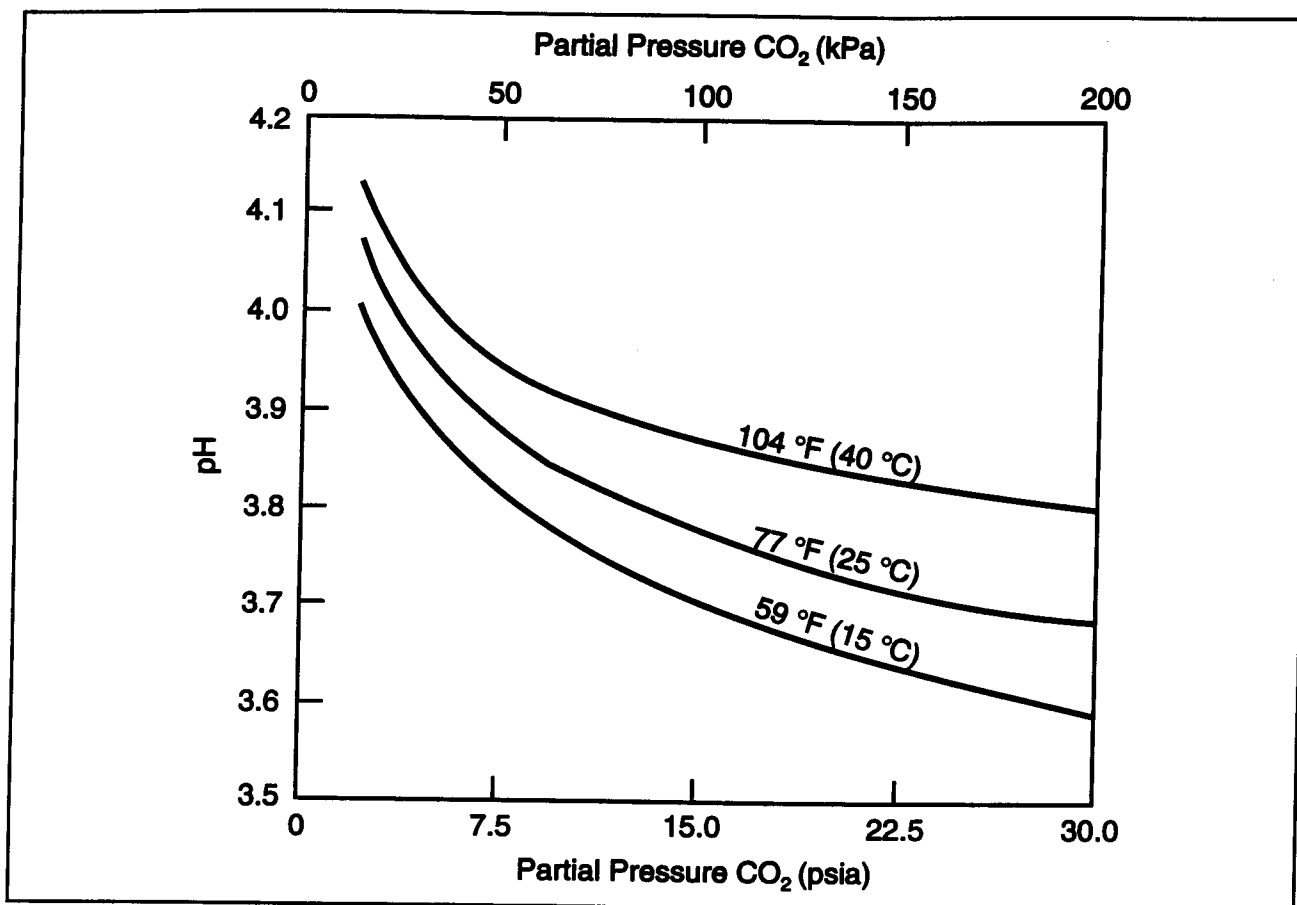


Figure 3.2 Effect of CO₂ Partial Pressure on the pH of Water (3.2)

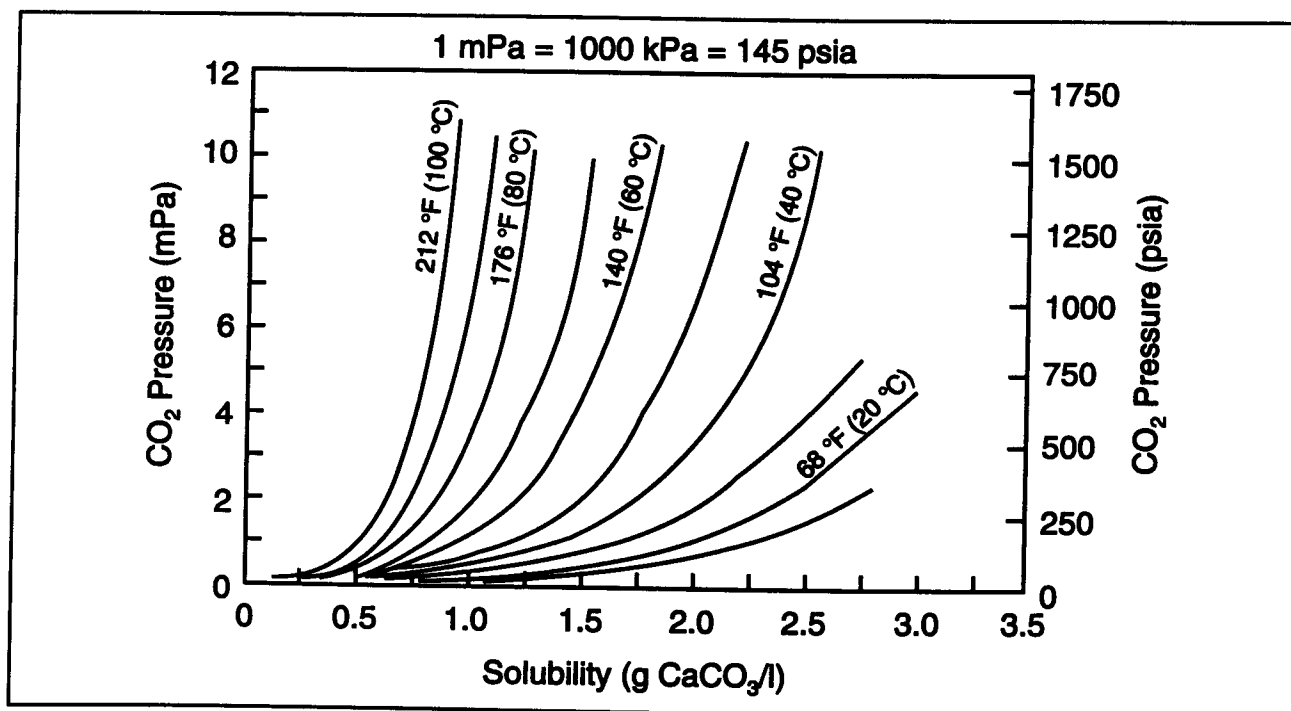


Figure 3.3 Effect of CO₂ Pressure on Calcium Carbonate Solubility (3.3)

Effect of Total Pressure

The solubility of calcium carbonate in a two phase system increases with increased pressure for two reasons:

- Increased pressure increases the partial pressure of CO_2 and increases the solubility of CaCO_3 in water as previously explained.
- Increased pressure also increases the solubility due to thermodynamic considerations which will not be discussed here.
- Pressure drops are one of the primary causes of calcium carbonate scale deposition in production systems. In addition to decreasing the solubility of CaCO_3 due to the loss of CO_2 and the thermodynamic pressure effect, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

In single phase (all water) systems, such as a water injection system, increased pressure increases the solubility of calcium carbonate solely due to thermodynamic considerations.

Effect of Temperature

Contrary to the behavior of most materials, calcium carbonate becomes less soluble as temperature increases — the hotter the water gets, the more likely CaCO_3 scale will form.

Hence, a water which is non-scaling at the surface may result in scale formation in an injection well if the downhole temperature is sufficiently high. This is also the reason that CaCO_3 scale is often found on the fire-tubes of heating equipment.

The solubility of CaCO_3 in pure water at 1 atmosphere CO_2 partial pressure as a function of temperature is shown in Figure 3.4.

Methods for calculating the temperature at which CaCO_3 scale may be anticipated are given in a later section.

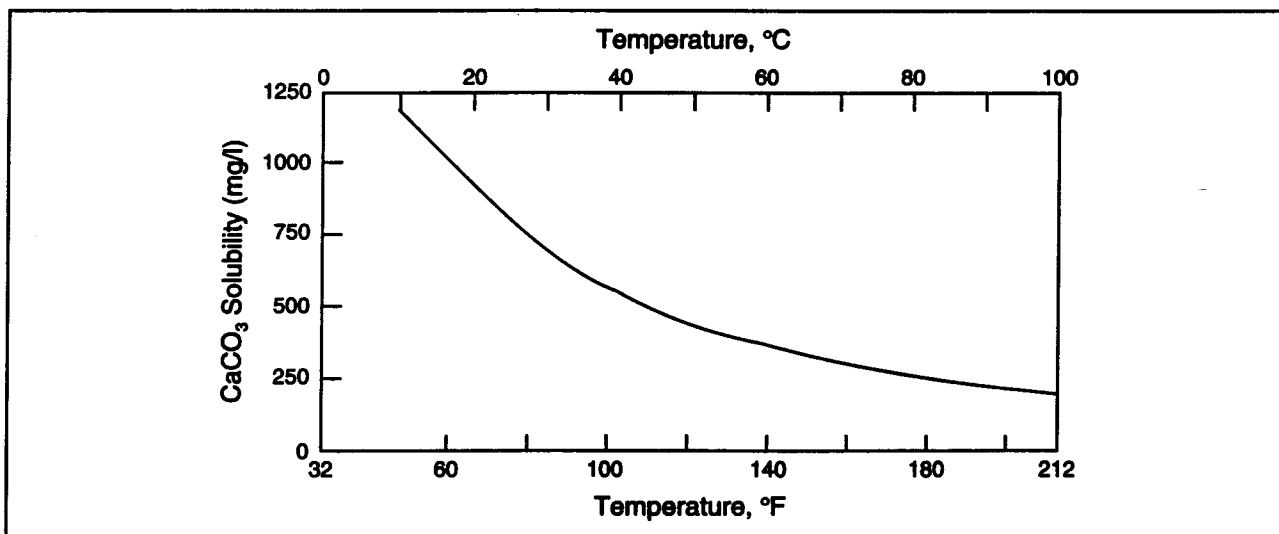


Figure 3.4 Calcium Carbonate Solubility^(3.3)

Effect of Dissolved Salts

Calcium carbonate solubility increases as the salt content of the water increases. For instance, adding 200 000 mg/L NaCl to distilled water increases the CaCO_3 solubility from 100 mg/L to 250 mg/L.

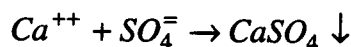
Actually, the higher the total dissolved solids (not counting calcium or carbonate ions), the greater the solubility of CaCO_3 in the water and the lower the scaling tendency up to a maximum of about 200 000 mg/L.

In summary, the likelihood of forming calcium carbonate scale:

- Increases with temperature
- Increases as partial pressure of CO_2 decreases
- Increases as the pH increases
- Increases as total dissolved salts decreases
- Increases as the total pressure decreases

Calcium Sulfate

The precipitation of calcium sulfate from water results from the reaction:



Forms of Calcium Sulfate

Most calcium sulfate deposits found in the oilfield are gypsum. According to Oddo and Tomson, the most likely scale to form from brines will be gypsum at temperatures less than 176°F [80°C].^(3,4)

Between 176°F [80°C] and 250 F [121°C], any of the three types of calcium sulfate may form, with gypsum being more likely at the low end of the temperature range and anhydrite more likely at the high end. Hemi-hydrate is commonly found in this temperature range in non-turbulent systems with high ionic strengths.

Above 250°F [121°C], any calcium sulfate scale formed will almost certainly be anhydrite.^(3,4)

Effect of Temperature

Gypsum solubility in pure water increases with temperature up to about 100°F [38°C], then decreases with temperature as shown in Figure 3.5.

This is quite different from the temperature-solubility behavior of CaCO_3 . First, gypsum is considerably more soluble than CaCO_3 in the normal temperature range of interest. Second, the maximum in the gypsum curve tells us that an increase in temperature could either increase or decrease the solubility of gypsum depending on which part of the temperature curve we're concerned with. This is decidedly different from CaCO_3 where an increase in temperature always decreases the solubility.

Note that above about 100°F [38°C], anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of CaSO_4 in deeper, hotter wells. Actually, the temperature at which the scale changes form from gypsum to anhydrite or hemi-hydrate is a function of many factors, including pressure, dissolved salt content, flow conditions, and the speed at which different forms of CaSO_4 can precipitate from solution.

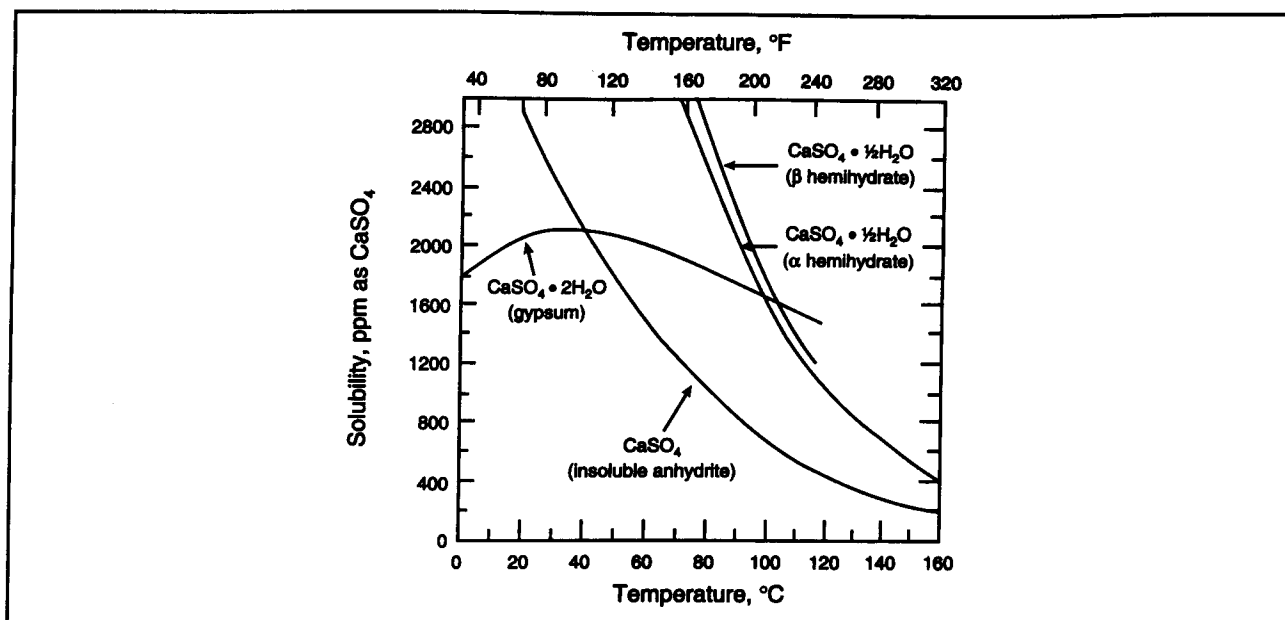


Figure 3.5 Solubility of Calcium Sulfate in Pure Water ^(3.5)

Predicting which form of calcium sulfate will precipitate under a given set of conditions is very difficult. Even though anhydrite would be expected above 100°F [38°C] in preference to gypsum due to its lower solubility, gypsum may be found at temperatures up to 212°F [100°C].

It is often difficult to precipitate anhydrite directly from solution. However, with the passage of time, gypsum can dehydrate to form anhydrite.

Above 212°F [100°C], anhydrite will precipitate directly in a stirred or flowing system. If the system is quiescent, hemi-hydrate solubility becomes limiting.^(3.6) Conversion to anhydrite could be expected with time.

Effect of Dissolved Salts

The presence of NaCl or dissolved salts other than calcium or sulfate ions increases the solubility of gypsum or anhydrite just as it does for CaCO_3 up to a salt concentration of about 150 000 mg/L. Further increases in salt content decrease CaSO_4 solubility. (Figure 3.6)

Effect of Pressure

Increased pressure increases the solubility of all forms of calcium sulfate due to thermodynamic considerations which will not be discussed here.^(3.7,3.8)

Pressure drops are one of the primary causes of calcium sulfate scale deposition in production systems. In addition decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

The effect of pressure and temperature on anhydrite solubility is shown in Figure 3.7. Note that the pressure effect decreases as temperature increases.

Effect of pH

pH has little or no effect on the solubility of calcium sulfate.

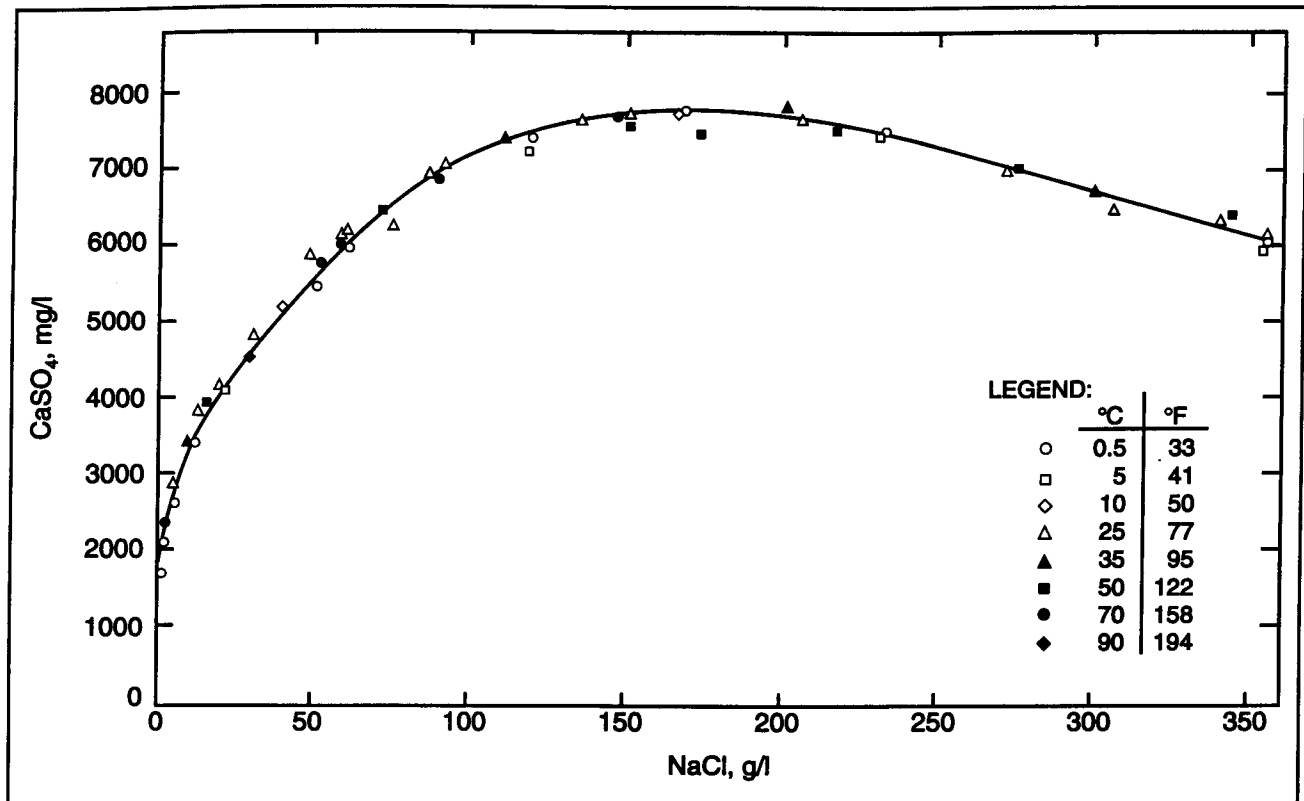


Figure 3.6 Solubility of Gypsum in NaCl Brines^(3.6)

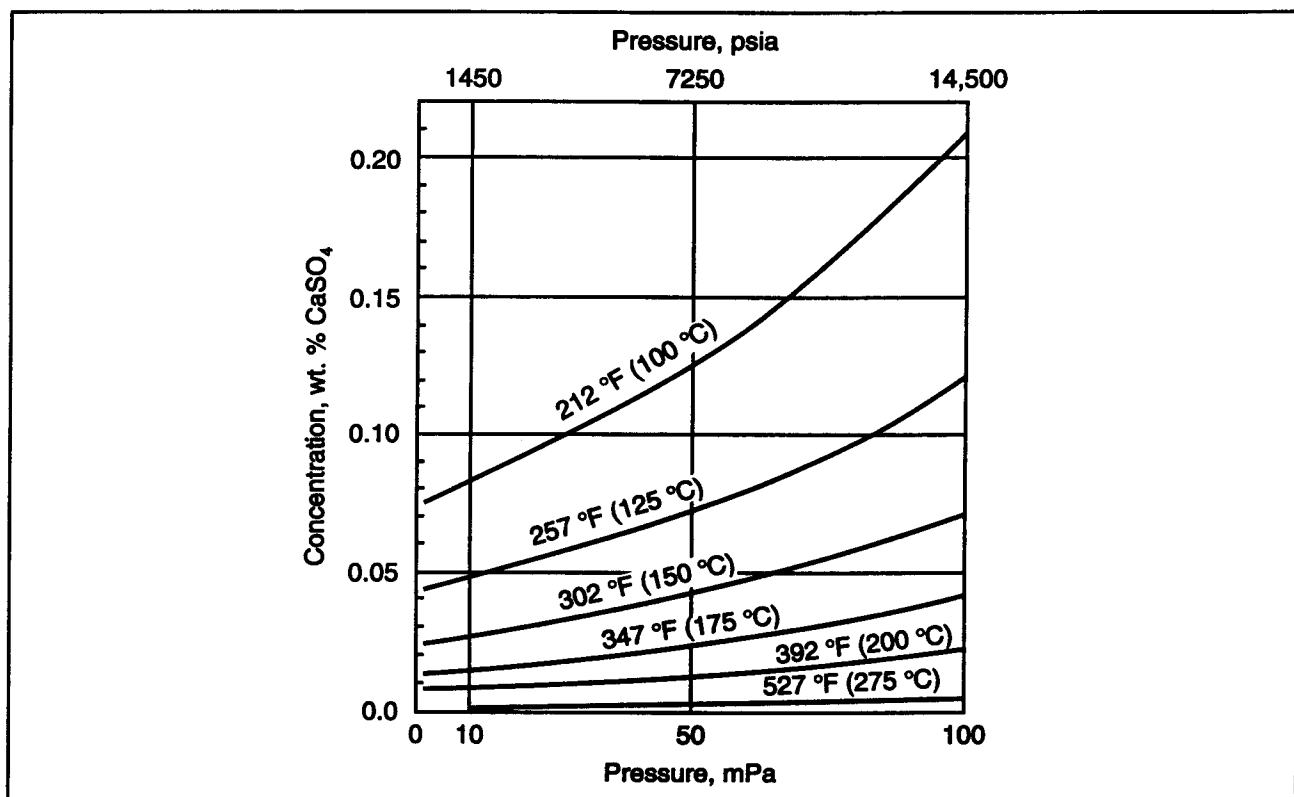


Figure 3.7 Effect of Pressure and Temperature on CaSO_4 (Anhydrite) Solubility^(3.9)

Barium Sulfate

Barium sulfate is the least soluble of the scales we have discussed thus far.

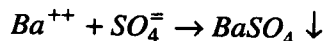


Table 3.2 compares the solubility of the three scales mentioned thus far, in distilled water at 77°F [25°C]:

TABLE 3.2
Comparative Solubilities at 25°C

Scale	Solubility (mg/L)
Gypsum	2080
Calcium Carbonate	53
Barium Sulfate	2.3

The extreme insolubility of BaSO_4 makes it very likely that scaling will occur if both Ba^{++} and SO_4^- ions are present in a water.

Most barium sulfate scales also contain some strontium sulfate.

Effect of Temperature

Barium sulfate solubility increases with temperature up to 212°F [100°C]. The solubility in distilled water increases from 2.3 mg/L at 77°F [25°C] to 3.9 mg/L at 203°F [95°C] as shown in Figure 3.8.^(3.10) The increase is fairly substantial percentage wise, but barium sulfate is still quite insoluble even at this higher temperature.

Above 212°F [100°C] the solubility decreases with temperature in waters with TDS values less than about 50 000 ppm. The solubility in higher salinity waters shows normal solubility behavior and increases with temperature as shown in Figure 3.9.^(3.11)

Because of the increase in solubility over normal temperature ranges, barium sulfate usually presents no downhole scaling problems in an injection well if it is non-scaling at surface conditions. It is more commonly a problem in producing or water-supply wells.

Effect of Dissolved Salts

The solubility of barium sulfate in water is increased by foreign dissolved salts just as in the case of calcium carbonate and calcium sulfate. The addition of 100 000 mg/L of NaCl to distilled water increases the solubility of BaSO_4 from 2.3 mg/L to 30 mg/L at 77°F [25°C]. Maintaining 100 000 mg/L NaCl and increasing the temperature to 203°F [95°C] will increase the BaSO_4 solubility to about 65 mg/L.^(3.1)

Figures 3.8 and 3.9 illustrates the effect of salinity on BaSO_4 solubility over a wide range of temperatures. The data in Figure 3.8 is plotted as a function of molar ionic strength rather than sodium chloride concentration. An ionic strength of 1.0 is equivalent to a sodium chloride concentration of approximately 60 000 mg/L. Ionic strength is defined later in this chapter and an example calculation is given in Appendix 14.

As a rule of thumb, you can assume that BaSO_4 solubility will double as the temperature is raised from 77°F [25°C] to 203°F [95°C] regardless of the dissolved salt concentration. The effect of dis-

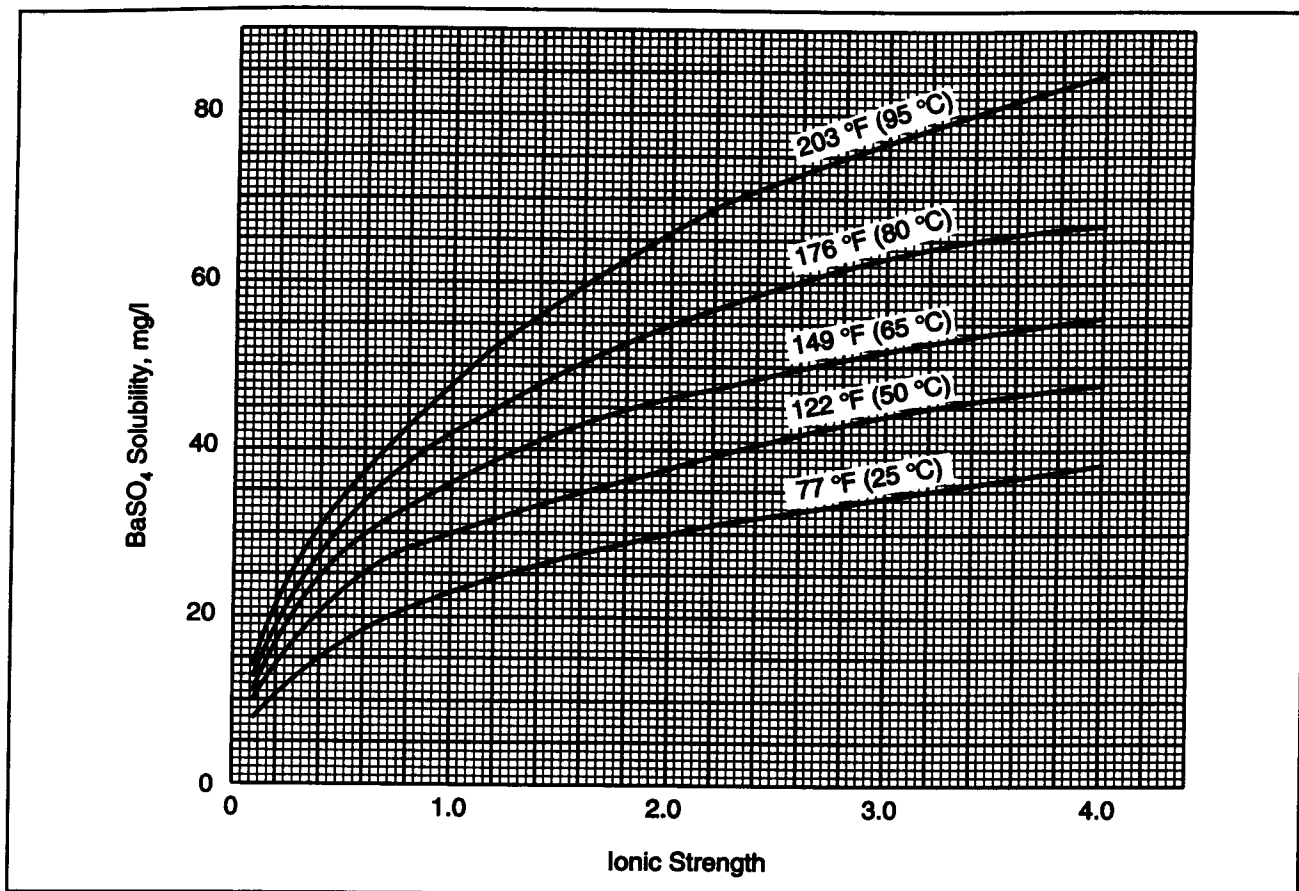


Figure 3.8 Barium Sulfate Solubility in NaCl Solutions Calculated from Templeton's Data^(3.10)

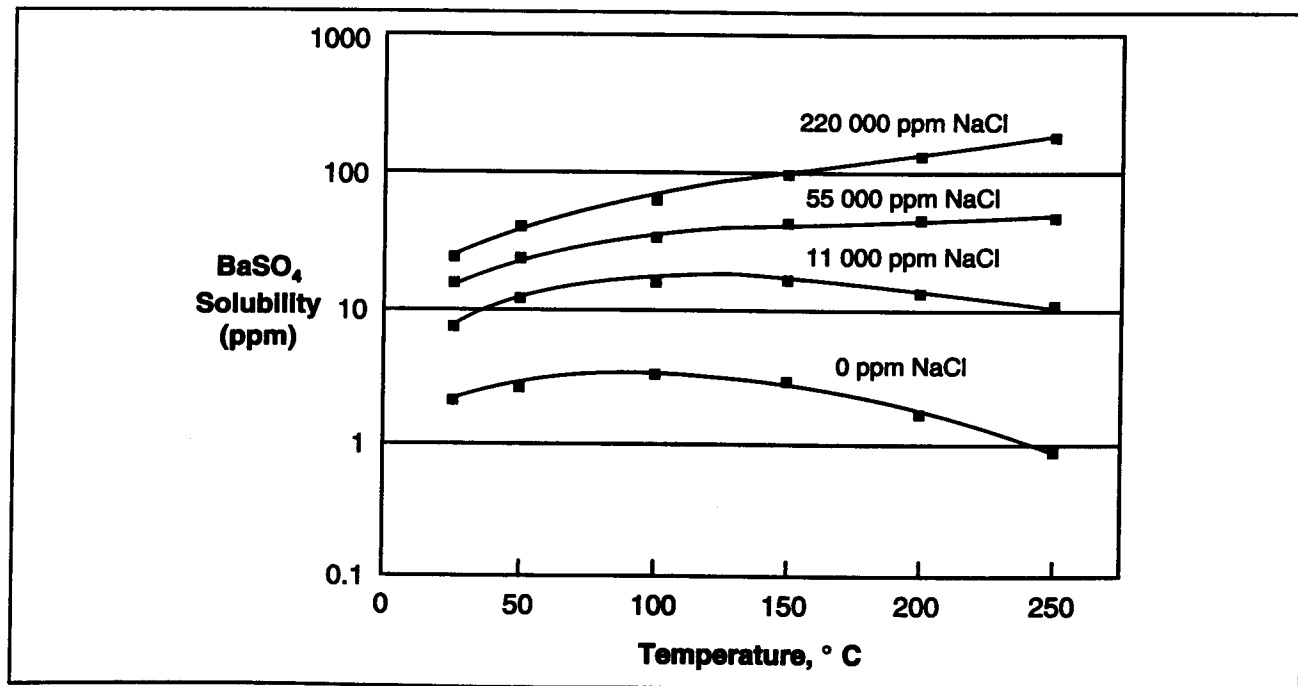


Figure 3.9 Effect of Temperature and Salinity on Barium Sulfate Solubility at Atmospheric Pressure^(3.11)

solved salts is much more pronounced, as demonstrated by the 13-fold increase brought about by the addition of 100 000 mg/L NaCl with no change in temperature.

Effect of Pressure

Increased pressure increases the solubility of barium sulfate due to thermodynamic considerations which will not be discussed here.

Pressure drops are one of the primary causes of barium sulfate scale deposition in production systems. In addition decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

Increased pressure increases the solubility of BaSO_4 . Figure 3.10 shows the effect of pressure and temperature on barium sulfate solubility in pure water.

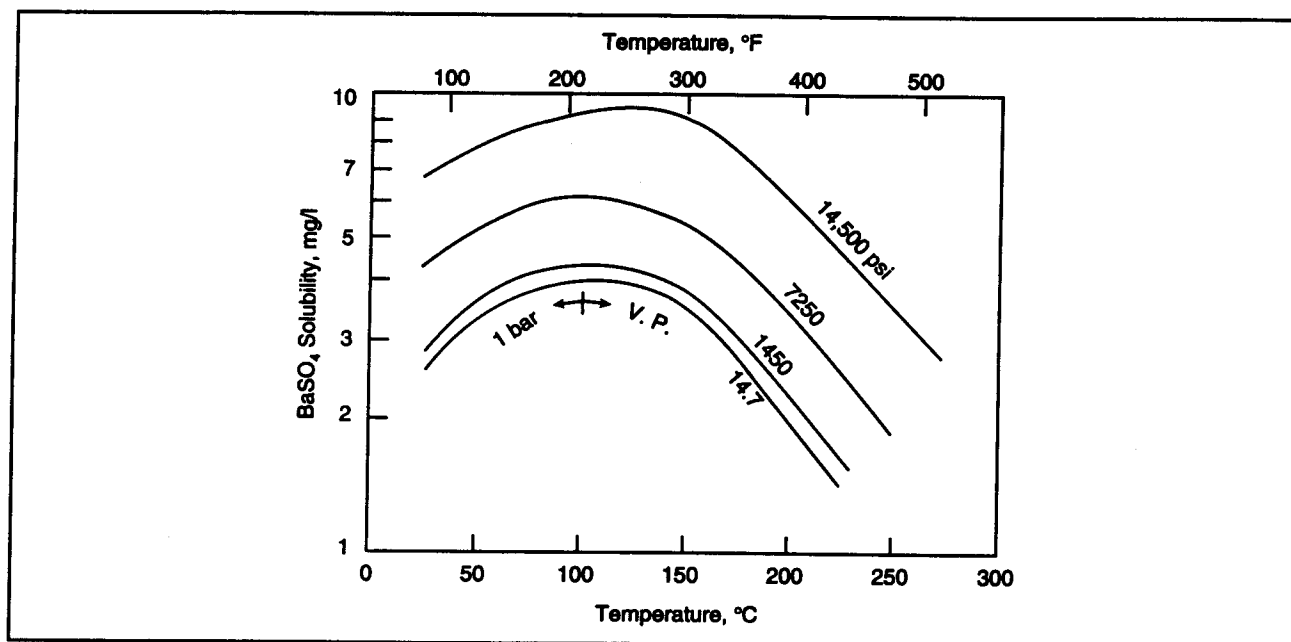


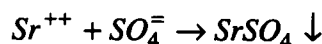
Figure 3.10 Effect of Pressure and Temperature on Barium Sulfate Solubility in Pure Water^(3.11)

Effect of pH

pH has little or no effect on the solubility of barium sulfate.

Strontium Sulfate

Strontium sulfate is considerably more soluble than barium sulfate, with a solubility of 129 mg/L in pure water at a temperature of 77°F [25°C].^(3.12)



Effect of Temperature

Strontium sulfate solubility decreases with temperature.^(3.12-3.14) In pure water the solubility decreases to 68 mg/L at 257°F [125°C].^(3.12)

Effect of Dissolved Solids

The solubility of SrSO_4 in water increases as the NaCl content of the water increases up to a maximum of approximately 175 000 mg/L. Further increases in salinity result in decreased solubility.^(3.12-3.16) In brines containing calcium or magnesium, the apparent solubility of SrSO_4 is greater than a NaCl brine of equivalent ionic strength.

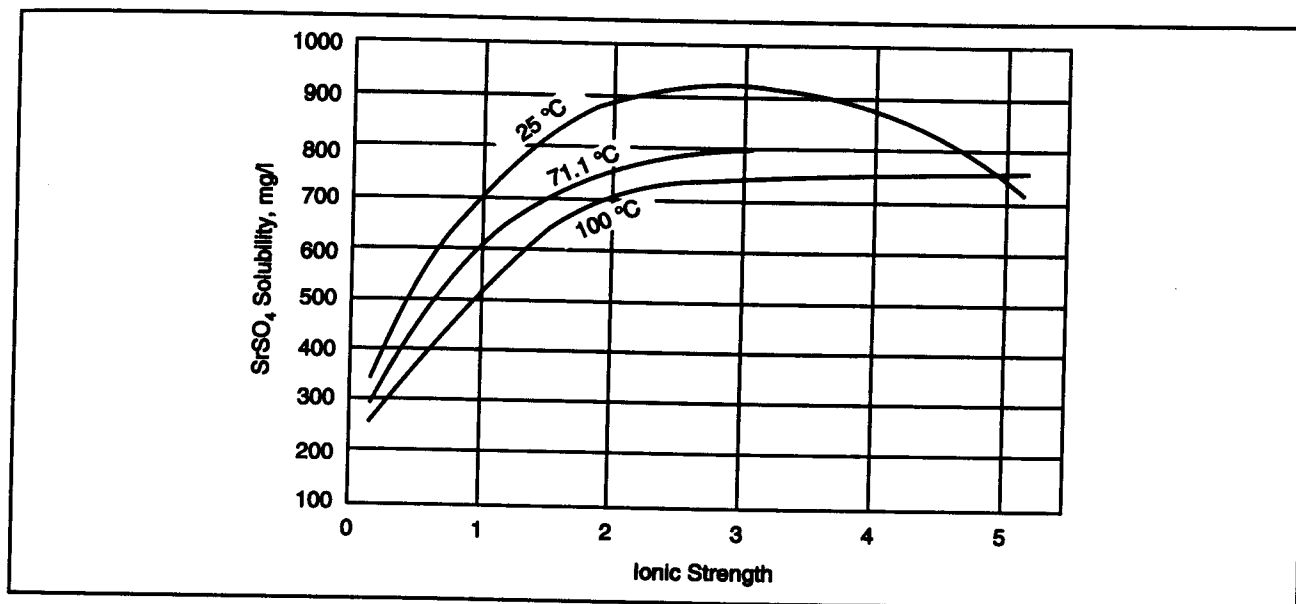


Figure 3.11 Strontium Sulfate Solubility in NaCl Solutions^(3.15)

Effect of Pressure

Strontium sulfate solubility in NaCl brines increases with pressure. However, solubility data measured by Jacques and Bourland show that the increase is small up to 3000 psig.^(3.13)

Pressure drops are one of the primary causes of strontium sulfate scale deposition in production systems. In addition to decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

Until the advent of seawater injection in the Middle East, pure SrSO_4 scale was seldom observed and was not considered a major problem in water injection operations. However, serious SrSO_4 scale problems have occurred in producing wells in a number of Middle East fields after breakthrough of seawater, due to mixing of the sulfate-bearing seawater and the strontium in the formation waters in the producing wellbores.^(3.17-3.19)

In the majority of cases, however, strontium co-precipitates with barium to form $(\text{Ba},\text{Sr}) \text{SO}_4$ scale. A study of several barium sulfate scales by Weintritt and Cowan^(3.20) showed strontium sulfate contents of 1.2 to 15.9 percent. Barium sulfate concentrations varied from 63.7 to 97.5 percent.

Unfortunately, we have no solubility data on electrolytes containing both barium and strontium.

Effect of pH

pH has little or no effect on the solubility of strontium sulfate.

Iron Compounds

Iron ions present in a water may be either naturally present in the water or the result of corrosion. Formation waters normally contain only a few mg/L of natural iron and values as high as 100 mg/L are rare. Higher iron contents are invariably the result of corrosion. Precipitated iron compounds are a common cause of deposit formation and injection well plugging, as well as being indicative of the equally serious problem of corrosion.

Corrosion is usually the result of CO_2 , H_2S or oxygen dissolved in the water. Most of the scales containing iron are corrosion products. However, iron compounds can also form by precipitation of natural formation iron even if corrosion is relatively mild.

Carbon dioxide can react with iron to form iron carbonate scale. Whether or not scale actually forms will depend on the pH of the system. Scale formation is much more likely above pH 7. Figure 3.12 illustrates the solubility of iron carbonate in fresh water.

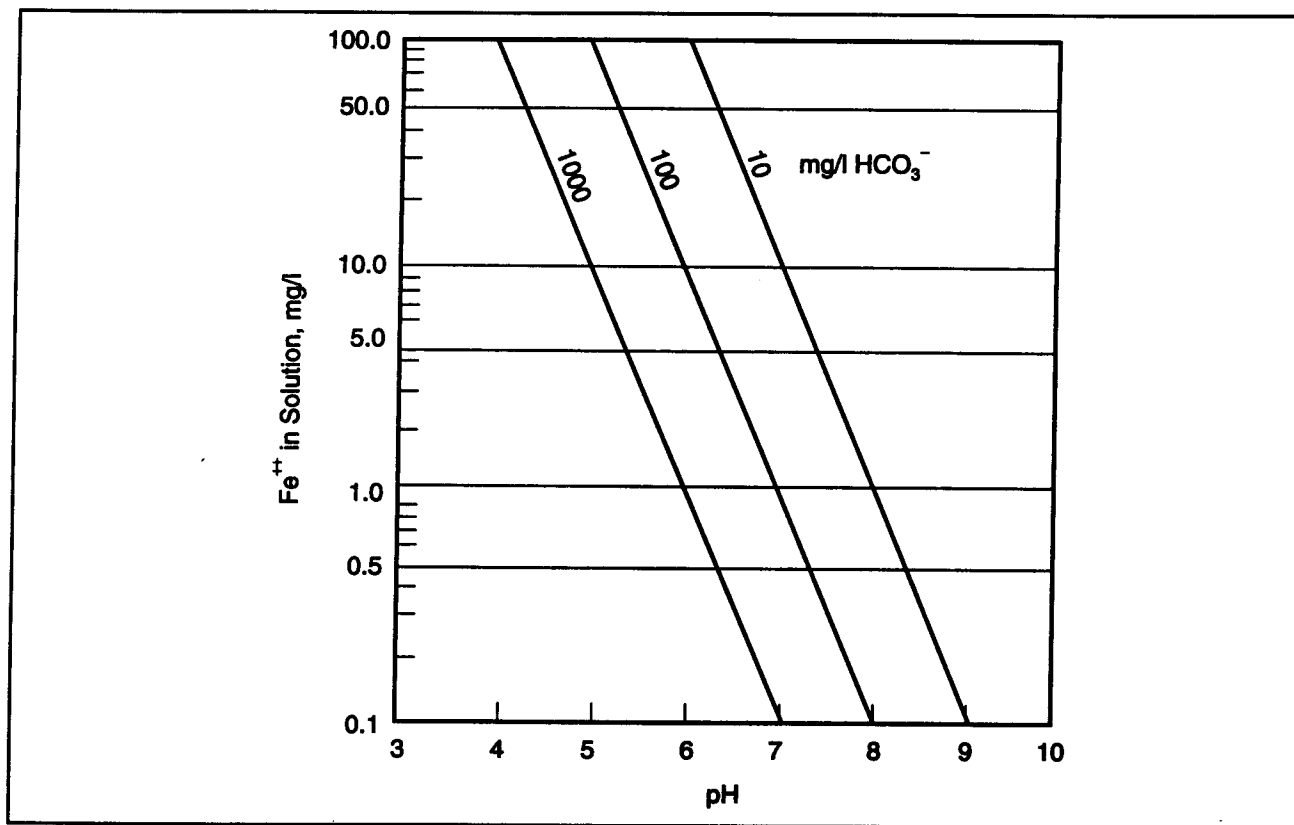


Figure 3.12 Iron Carbonate Stability Diagram

Hydrogen sulfide will form iron sulfide as a corrosion product which is quite insoluble and usually forms a thin, adherent scale. Suspended iron sulfide is the cause of "black water."

The iron sulfide diagram in Figure 3.13 illustrates the concentration of Fe^{++} (ferrous ion) which will stay in solution at various pH values and H_2S concentrations in fresh water. Fe^{+++} (ferric ion) is seldom found at pH values above 3.0.

Oxygen combines to form several compounds. Ferrous hydroxide, $\text{Fe}(\text{OH})_2$, ferric hydroxide, $\text{Fe}(\text{OH})_3$, and ferric oxide, Fe_2O_3 , are common scales resulting from contact with air. For example,

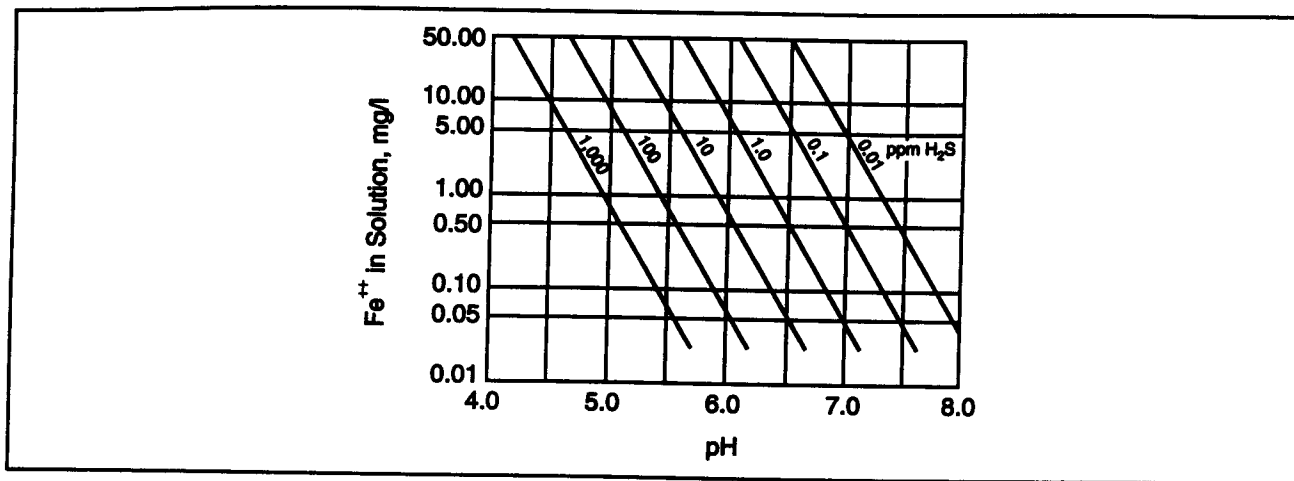
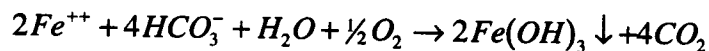


Figure 3.13 Iron Sulfide Stability Diagram

when air-free water containing dissolved ferrous iron ions and bicarbonate ions is contacted by air, ferric hydroxide can be formed.



Ferrous iron (Fe^{++}) is oxidized by the presence of air to give Fe^{+++} , and ferric hydroxide results. This is practically insoluble above pH 4. As shown in Figure 3.14, if oxygen can be excluded, 100 ppm of $\text{Fe}(\text{OH})_2$ (ferrous hydroxide) will still be in solution at pH 8.5.

“Red water” is the result of suspended particles of Fe_2O_3 , another product of oxygen and iron.

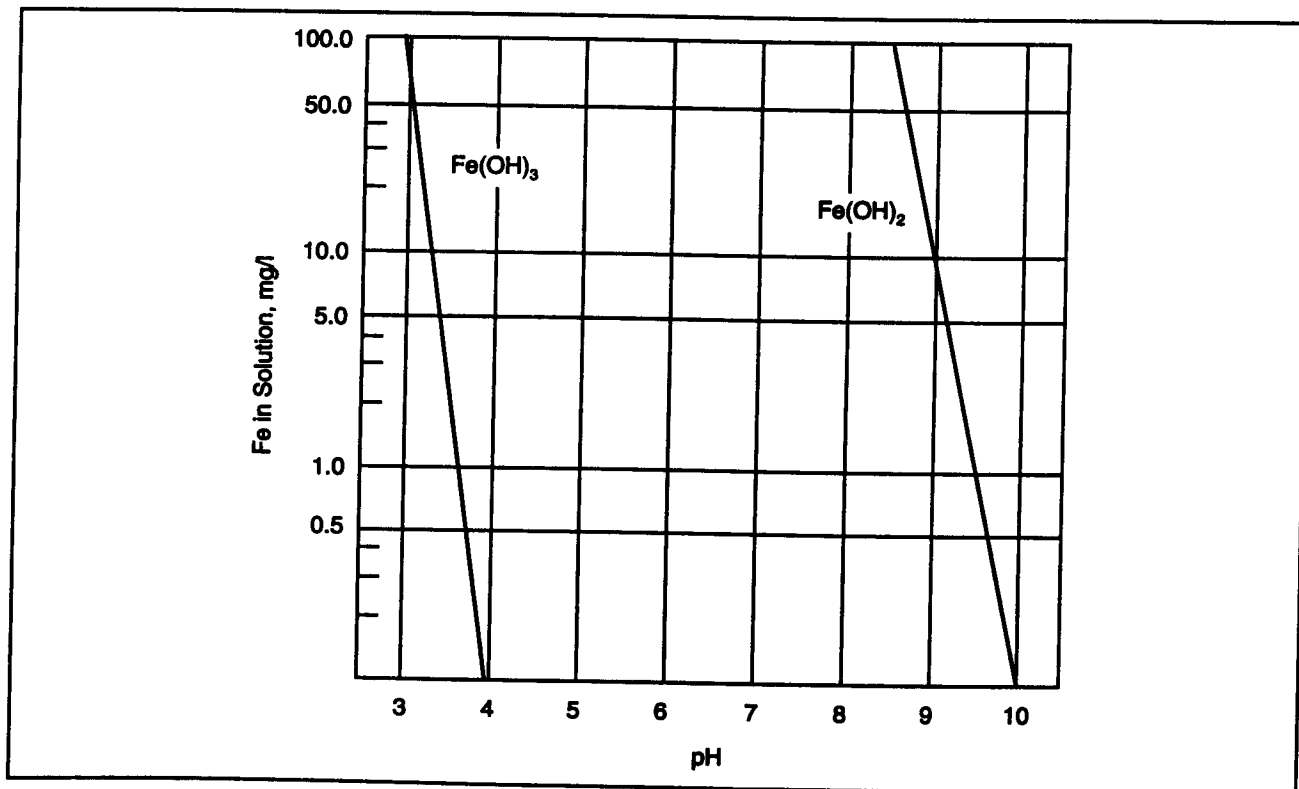


Figure 3.14 Iron Hydroxide Stability Diagram

Iron compounds can also result from the action of certain bacteria (*Gallionella ferruginea*) which live in water in the presence of air. These bacteria take Fe^{++} ions from the water and deposit ferric hydroxide.

In summary, the chemistry of iron compounds is much more complex than that of previously discussed compounds. This is due primarily to the fact that iron commonly exists in two oxidation states in water, Fe^{++} (ferrous) and Fe^{+++} (ferric). These two ions form compounds with the same anions that possess very different solubilities. It is difficult to quantitatively predict the behavior of iron compounds. It is far more important to prevent their formation — a topic which will be covered in a later section.

Silica Deposits

Silica deposits are not common in produced waters or in injection projects. However, they can be quite serious in boilers and steam generators, and are sometimes a problem in cooling waters.

Silica is thought to occur in both the colloidal state as SiO_2 , or it can combine with magnesium, sodium or aluminum ions to form silicate scales. It can also vaporize in steam boilers and then precipitate on turbine blades. Because of the complexity of this behavior, it is difficult to predict the conditions under which silica can be kept in solution.

NORM

Naturally occurring radioactive materials (NORM) are found in many production and injection systems. Of interest are scales which are radioactive due to the presence of Ra-226 and Ra-228 ions which have co-precipitated from produced water along with scale-forming cations during scale formation. The radium ions are trapped within the crystal lattice of the material.

NORM has been commonly associated with barium sulfate scales. However, in practice, any scale or corrosion product may contain co-precipitated radium ions and be radioactive.

PREDICTING SCALE FORMATION

The Value of Solubility Calculations

Solubility calculations or scaling indexes may be used to predict the formation of certain types of scales. The values obtained from these calculation procedures should be taken merely as guidelines. They indicate the degree of "scaling tendency," or the likelihood of scale formation. Simplifying assumptions have been made in the derivation of each equation; solubility in naturally occurring waters is a complex phenomenon.

It should be emphasized that if scale formation is indicated by calculation, it serves as an alarm. If you are looking at a possible water source, you should avoid those which show scaling tendencies or make provision for treatment in your planning. Similarly, one should avoid mixing waters which would result in a composite analysis which exhibits scaling tendencies under system conditions.

A calculated scaling tendency in an existing system should focus attention on the fact that scale formation is likely and you should begin inspecting the system for signs of scale formation immediately. Solubility calculations are an extremely valuable tool, but like nearly everything else, their absolute value will be greatly influenced by the user's experience and judgment.

The following section is a summary of some of the published scale prediction equations which are commonly used for oilfield waters. No attempt has been made to include all of the published solubility information

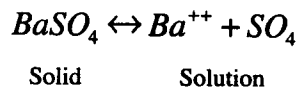
The Basis for Solubility Calculations

All scale prediction methods are based on laboratory measurements of the solubility of a specific compound at equilibrium conditions. Normally, solubilities are measured in synthesized waters over a range of temperatures at atmospheric pressure.

Solubility Product Principle

When a sparingly soluble salt is added to water, cations and anions from the crystal lattice of the solid pass into solution until the solution becomes saturated. In the saturated solution an equilibrium exists between the ions in solution and ions present in the solid crystal lattice.

Using barium sulfate (BaSO_4) as an example:



At a given temperature and pressure the product of the activities of the ions in the saturated solution is constant and is called the *thermodynamic solubility product constant*, K_{sp} .

$$K_{sp} = a_{\text{Ba}^{++}} \times a_{\text{SO}_4^-} \quad (3.8)$$

Where: $a_{\text{Ba}^{++}}$ = Barium ion activity
 $a_{\text{SO}_4^-}$ = Sulfate ion activity

The activity of an ion is defined as the product of the ion concentration and the activity coefficient.

$$a_{\text{Ba}^{++}} = C_{\text{Ba}^{++}} \times \gamma_{\text{Ba}^{++}} \quad (3.9)$$

$$a_{\text{SO}_4^-} = C_{\text{SO}_4^-} \times \gamma_{\text{SO}_4^-} \quad (3.10)$$

Where: $C_{\text{Ba}^{++}}$ = Ba^{++} concentration, moles/L
 $C_{\text{SO}_4^-}$ = SO_4^- concentration, moles/L

The activity coefficient is a function of temperature, pressure and ionic strength.

It is often convenient to include the activity coefficients in the solubility constant term so that the concentrations of the ions can be used in the equations rather than the activities. The resulting solubility product is then defined as the *ion product constant* or *conditional solubility product constant*, K_c , and is defined in Equation 3.11.

$$K_c = \frac{K_{sp}}{\gamma_{\text{Ba}^{++}} \times \gamma_{\text{SO}_4^-}} = (C_{\text{Ba}^{++}})(C_{\text{SO}_4^-}) \text{ at saturation} \quad (3.11)$$

Where: K_c = Conditional solubility product constant, molar units

Based on this principle, it is possible to evaluate a solution with respect to the possibility of the precipitation of a given salt at a given temperature and pressure by comparing the value of the ion product constant at those conditions with the product of the measured concentrations of the ions in the solution.

If we have a solution which contains a given amount of dissolved BaSO_4 , and the measured concentrations of Ba^{++} and $\text{SO}_4^{=}$ are $C_{\text{Ba}^{++}}$ and $C_{\text{SO}_4^{=}}$ respectively, the possibilities are as follows:

1. The solution is saturated with BaSO_4 .

$$(C_{\text{Ba}^{++}})(C_{\text{SO}_4^{=}}) = K_c \quad (3.12)$$

2. The solution is undersaturated with BaSO_4 . Precipitation cannot occur.

$$(C_{\text{Ba}^{++}})(C_{\text{SO}_4^{=}}) < K_c \quad (3.13)$$

3. The solution is supersaturated with BaSO_4 . Precipitation can occur.

$$(C_{\text{Ba}^{++}})(C_{\text{SO}_4^{=}}) > K_c \quad (3.14)$$

Thus, precipitation can occur only in the last case. However, it may not occur in practice due to the fact that solutions often remain supersaturated until sufficient energy is available to initiate nucleation of the crystalline solid from solution.

Saturation Ratio

Continuing with the example of BaSO_4 dissolved in water, the *saturation ratio* (sometimes called the supersaturation ratio) is defined as the ratio of the ion product to the ion product constant:

$$SR = \frac{IP}{K_c} = \frac{C_{\text{Ba}^{++}} \times C_{\text{SO}_4^{=}}}{K_c} \quad (3.15)$$

Where: IP = Ion product
 SR = Saturation Ratio
 $C_{\text{Ba}^{++}}$ and $C_{\text{SO}_4^{=}}$ = Measured concentration of Ba^{++} and $\text{SO}_4^{=}$ in solution

Thus, it is also possible to express the conditions necessary for precipitation in terms of the saturation ratio:

1. $SR = 1$ The solution is saturated with BaSO_4 .
2. $SR < 1$ The solution is undersaturated with BaSO_4 .
Precipitation cannot occur.
3. $SR > 1$ The solution is supersaturated with BaSO_4 .
Precipitation can occur.

Calcium Carbonate Scaling Calculations

Calcium Carbonate Saturation Indexes

It is common to express the degree of supersaturation, and hence the likelihood of precipitation of CaCO_3 from a solution in terms of the *saturation index*, which is defined as follows:

$$\text{Saturation Index} = \log_{10} \left[\frac{IP}{K_c} \right] \quad (3.16)$$

Although there is agreement as to the definition of the saturation index, different investigators have used different nomenclature to describe the term.

TABLE 3.3
Calcium Carbonate Saturation Indexes

Investigator	Index Name	Abbreviation
Langelier ^(3.21)	Saturation Index	SI
Ryznar ^(3.22)	Stability Index	SI
Stiff & Davis ^(3.23)	Stability Index	SI
Oddo & Tomson ^(3.24)	Saturation Index	I _s

The saturation index, which we will refer to as SI, is a measure of the degree of supersaturation, and thus the driving force available to cause precipitation. The larger the value of SI, the greater the likelihood that scale will occur. It does not predict the amount of scale which will precipitate.

Figure 3.15 illustrates the relationship between the supersaturation ratio and the saturation index:

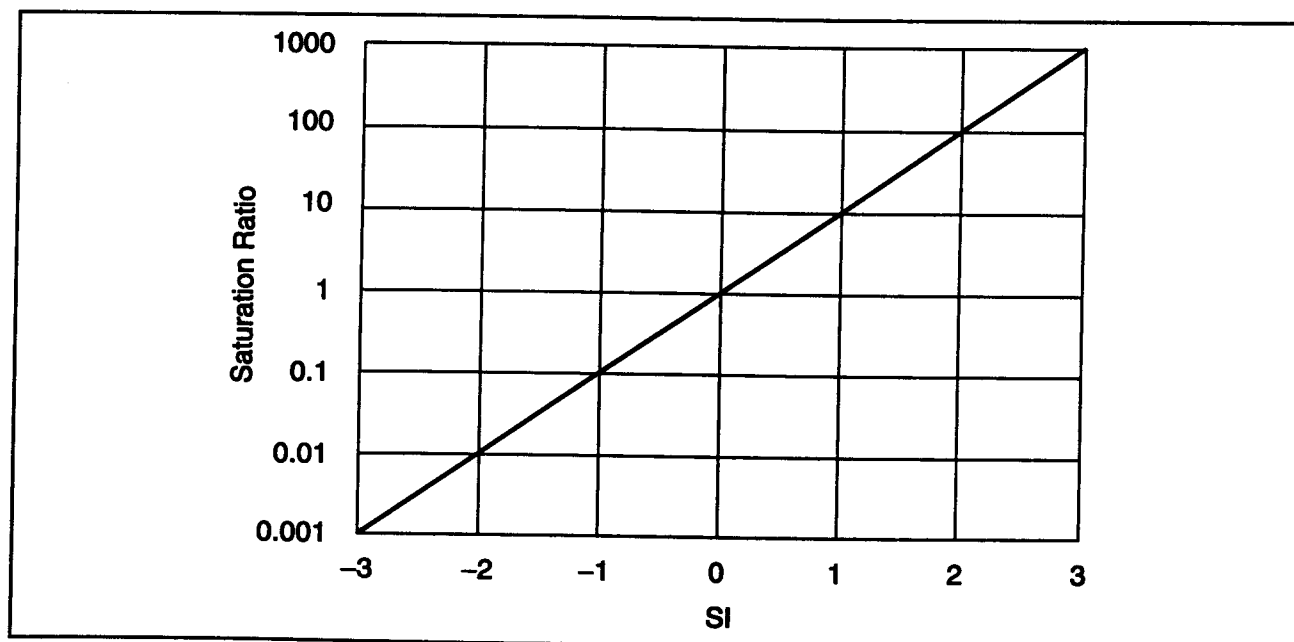


Figure 3.15 Saturation Index (SI) vs Saturation Ratio (SR)

Langelier Saturation Index^(3.21)

This well known index was developed to predict whether a fresh water saturated with dissolved oxygen would form calcium carbonate scale or be corrosive.

The Langelier saturation index is calculated from the following empirical equation:

$$\begin{array}{lcl} SI & = & pH - pH_s \\ \text{Stability} & & \text{Actual pH} \\ \text{Index} & & \text{of Water} \end{array} \quad \begin{array}{l} - \\ \\ \end{array} \quad \begin{array}{l} pH_s \\ \\ \text{pH at which} \\ \text{water would be} \\ \text{saturated with} \\ \text{CaCO}_3 \end{array} \quad (3.17)$$

$$pH_s = pCa + pAlk M + C_t \quad (3.18)$$

$$pCa = \log \frac{1}{\text{Moles Ca}^{++} / \text{Liter}} \quad (3.19)$$

$$pAlk M = \log \frac{1}{\text{Equivalents M Alkalinity} / \text{Liter}} \quad (3.20)$$

$$M \text{ Alkalinity} = \text{Total Alkalinity} = \text{CO}_3^- + \text{HCO}_3^-, \text{ equivalents} / L \quad (3.21)$$

Where: C_t = a constant which is a function of the Total Dissolved Solids and temperature

As previously explained, if $SI > 0$, precipitation of CaCO_3 is indicated. A negative value of SI indicates that the water is corrosive if dissolved oxygen is present. This index indicates the tendency of a water to precipitate calcium carbonate, but it does not indicate the amount of precipitate.

Values of the empirical constants used to solve these equations are given elsewhere for molal ionic strengths of 0-0.02 [0-800 ppm TDS] and temperatures of 32-194°F [0-90°C] at atmospheric pressure.^(3.21)

The nomograph developed by Caplan^(3.25) is reproduced in Appendix 11 and permits easy determination of the Langelier Index.

Ryznar Stability Index^(3.22)

Ryznar developed an empirical equation for calculating the "stability index" of fresh water at atmospheric pressure. This index not only indicates the tendency of a water to precipitate calcium carbonate (or be corrosive if it is saturated with oxygen), it also gives a semi-quantitative estimate of the amount of scale which will form or the seriousness of the corrosion.

$$SI = 2pH_s - pH \quad (3.22)$$

Ryznar's stability index values always are positive. They can be interpreted as follows:

- Stability Index < 6.5 indicates CaCO_3 scale formation. The smaller the index, the larger the amount of scale indicated.
- Stability Index > 6.5 indicates corrosion if dissolved oxygen is present. The larger the index, the more severe the anticipated corrosion.

Caplan's nomograph in Appendix 11 can be used to determine the Ryznar Index.

Stiff and Davis Method^(3.23)

Stiff and Davis empirically extended the Langelier method to apply to oilfield brines. Their equation is as follows:

$$\begin{array}{ccccc} SI & = & pH & - & pHs \\ \text{Stability} & & \text{Actual pH} & & \text{pH at which} \\ \text{Index} & & \text{of Water} & & \text{water would be} \\ & & & & \text{saturated with} \\ & & & & \text{CaCO}_3 \end{array} \quad (3.23)$$

$$pHs = K + pCa + pAlk \quad (3.24)$$

Therefore:

$$SI = pH - K - pCa - pAlk \quad (3.25)$$

Where:

- SI = Stability Index. If SI is negative, the water is undersaturated with CaCO_3 and scale formation is unlikely. If SI is positive, scale is likely to form.
- pH = Actual pH of the water
- K = A constant which is a function of salinity, composition and water temperature. Values of K are obtained from a graphical correlation with ionic strength and the temperature of the water.

$$pCa = \log \frac{1}{\text{Moles Ca}^{++} / \text{Liter}} \quad (3.26)$$

$$pAlk \text{ } M = \log \frac{1}{\text{Equivalents } M \text{ Alkalinity} / \text{Liter}} \quad (3.27)$$

$$M \text{ Alkalinity} = \text{Total Alkalinity} = \text{CO}_3^{=} + \text{HCO}_3^{-}, \text{ mg / L} \quad (3.28)$$

The ionic strength is:

$$\mu = \frac{1}{2} (C_1 Z_1^2 + C_2 Z_2^2 + C_3 Z_3^2 + \dots + C_n Z_n^2) \quad (3.29)$$

Where:

- C = Concentration of the ion in moles/liter.
- Z = Valence of the ion

In order to calculate SI we must know the temperature, pH, and the HCO_3^{-} and $\text{CO}_3^{=}$ concentrations. In addition, a complete water analysis is necessary to enable calculation of the ionic strength.

It is essential that values of pH, HCO_3^{-} and $\text{CO}_3^{=}$ be measured in the field immediately after sampling, since these parameters change very quickly once the sample is removed from a pressurized system. Valid calculations cannot be made from laboratory analyses.

Unfortunately, even field measurements of pH values will not suffice when attempting to apply this method to downhole conditions in producing or injection wells. The pH must be calculated.

Equations are given in the following section which enable estimation of pH values at elevated pressures and temperatures.

Values of K as a function of ionic strength are given in Appendix 12. These curves are based on experimental data measured over the following range:

- Molar Ionic Strength: 0-3.6
- Temperature: 32, 86 and 122°F [0, 30 and 50°C]
- Pressure: 1 atmosphere [101.3 kPa]

All curves outside of this data range were extrapolated.

A chart for the determination of pCa and pAlk is given in Appendix 13.

The results of the calculation may be summarized as follows:

TABLE 3.4
Interpretation of Stiff & Davis Index

Case	Conclusion
SI is negative	The water is undersaturated with CaCO ₃ . Scale formation is unlikely.
SI is positive	The water is supersaturated with CaCO ₃ . Scale formation is indicated.
SI = 0	The water is saturated with CaCO ₃ .

An example calculation is given in Appendix 14.

Oddo and Tomson Method^(3.4,3.24, 3.26)

The equations developed by Oddo and Tomson enable the calculation of the saturation index, I_s , and considers the effect of total pressure as well as varying CO₂ partial pressures. Its meaning is analogous to that of the Stiff and Davis Index. They also developed equations which permit the calculation of pH.

Their initial work was published in 1982. The method was subsequently modified to include the effects of additional parameters. The equations given here were published in 1994.

Any System (Gas Phase Present or Absent) Where the pH is Known

$$I_s = \log \left[(Ca^{++})(HCO_3^-) \right] + pH - 2.76 + 9.88 \times 10^{-3} T + 0.61 \times 10^{-6} T^2 - 3.03 \times 10^{-5} P - 2.348 \sqrt{\mu} + 0.77 \mu \quad (3.30)$$

Where:

- Ca⁺⁺ = Calcium ion concentration, moles/L
- HCO₃⁻ = Bicarbonate ion concentration, moles/L
- T = Temperature, °F
- P = Total absolute pressure, psia
- μ = Molar ionic strength, moles/L

Gas Phase Absent

These equations are applicable in water injection systems and in production systems where the system pressure is greater than the bubble point pressure of the fluids.

1. Determine C_{aq} , the amount of CO_2 dissolved in the water. This can be determined directly by on-site titration, or it can be calculated using Equation 3.31.

$$\log C_{aq} = \log P_{CO_2} - 2.212 - 6.51 \times 10^{-3} T + 10.19 \times 10^{-6} T^2 - 1.29 \times 10^{-5} P - 0.77 \sqrt{\mu} - 0.059 \mu \quad (3.31)$$

2. Calculate I_s or the pH as desired.

$$I_s = \log \left[\frac{(Ca^{++})(HCO_3^-)^2}{C_{aq}} \right] + 3.63 + 8.68 \times 10^{-3} T + 8.55 \times 10^{-6} T^2 - 6.56 \times 10^{-5} P - 3.42 \sqrt{\mu} + 1.373 \mu \quad (3.32)$$

$$pH = \log \left[\frac{(HCO_3^-)}{C_{aq}} \right] + 6.39 - 1.198 \times 10^{-3} T + 7.94 \times 10^{-6} T^2 - 3.53 \times 10^{-5} P - 1.067 \sqrt{\mu} + 0.599 \mu \quad (3.33)$$

3. It is also possible to calculate the change in I_s or pH in a system without a gas phase using the following equations:

$$\Delta I_s = 8.68 \times 10^{-3} \Delta T + 8.55 \times 10^{-6} \Delta(T^2) - 6.56 \times 10^{-5} \Delta P \quad (3.34)$$

$$\Delta pH = -1.198 \times 10^{-3} \Delta T + 7.94 \times 10^{-6} \Delta(T^2) - 3.53 \times 10^{-5} \Delta P \quad (3.35)$$

Gas Phase is Present and the pH is Unknown

1. Calculate f_g , the fugacity coefficient of CO_2 gas.

$$f_g = \exp \left[P \times \left(2.84 \times 10^{-4} - \frac{0.255}{T + 460} \right) \right] \quad (3.36)$$

2. Calculate y_g , the mole or volume fraction of CO_2 in the gas phase at the specified T and P. Given that y_t is the mole fraction CO_2 in the gas at the surface.

$$y_g = \frac{y_t}{\left[1.0 + \frac{Pf_g (5.0BWP + 10.0BOPD) \times 10^{-5}}{MMscf(T + 460)} \right]} \quad (3.37)$$

Where: BOPD = Barrels of oil per day
 BWPD = Barrels of water per day
 MMscf = Million standard cubic feet of gas per day

3. Calculate the molar ionic strength.

$$\mu(\text{Moles/L}) = 10^{-5}(2.2 \times Na^{+} + 5.0 \times Ca^{++} + 8.2 \times Mg^{++} + 1.5 \times Ba^{++} + 2.3 \times Sr^{++} + 1.4 \times Cl^{-} + 2.1 \times SO_4^{-} + 0.8 \times HCO_3^{-}) \quad (3.38)$$

Where all ion concentrations are in mg/L and are obtained from a water analysis.

4. Calculate I_s or the pH as desired.

$$I_s = \log \left[\frac{(Ca^{++})(HCO_3^{-})^2}{Py_g f_g} \right] + 5.85 + 15.19 \times 10^{-3} T - 1.64 \times 10^{-6} T^2 - 5.27 \times 10^{-5} P - 3.334 \sqrt{\mu} + 1.431 \mu \quad (3.39)$$

$$pH = \log \left[\frac{(HCO_3^{-})}{Py_g f_g} \right] + 8.60 + 5.31 \times 10^{-3} T - 2.253 \times 10^{-6} T^2 - 2.237 \times 10^{-5} P - 0.99 \sqrt{\mu} + 0.658 \mu \quad (3.40)$$

This method is said to be valid over the following data range:

- Molar Ionic Strength: 0-4.0
- Temperature: 32-392°F [0-200°C]
- Pressure: 0-20 000 psig

Effect of Carboxylic Acids on CaCO₃ Saturation Index Calculations

Generally, alkalinity titrated to a pH of approximately 4.5 is assumed to be equal to the bicarbonate ion concentration. In produced waters, a substantial concentration of carboxylic acids (often called volatile fatty acids or "VFA's") is often present. As explained in Chapter 2, the acids are ionized in water and the species which are actually present are the VFA anions, which are typically dominated by the acetate ion. The VFA anions contribute to alkalinity.

The total alkalinity is as follows:

$$\text{Total Alkalinity} = HCO_3^{-} + \underset{\text{Acetate Ion}}{CH_3COO^{-}} + \underset{\text{Propionate Ion}}{CH_3CH_2COO^{-}} + \underset{\text{Butyrate Ion}}{CH_3CH_2CH_2COO^{-}}$$

In many cases, the acetate ion concentration is far larger than the concentration of the other VFA ions, so their presence can be ignored, and the alkalinity can be assumed to simply be the sum of the bicarbonate and acetate ion concentrations.

The acetate ion concentration can be determined by gas chromatography and the HCO_3^{-} concentration can then be approximated by the method proposed by Oddo and Tomson.^(3,4)

Failure to include the effect of VFA anions will result in a saturation index value more positive than would be calculated if the VFA anions were not subtracted from the total alkalinity.

Effect of H₂S on CaCO₃ Saturation Index Calculations

The presence of significant quantities of sulfides in produced water can also significantly effect saturation index values since bisulfide ion concentrations will be included in alkalinity values.

Assuming a sour brine at a pH less than 9 with no VFA anions present:

$$\text{Total Alkalinity} = \text{HCO}_3^- + \text{HS}^-$$

At a given pH, the HS⁻/HCO₃⁻ ratio in the water is approximately equal to the ratio of the partial pressures in the gas phase:^(3,4)

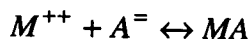
$$\frac{\text{HS}^-}{\text{HCO}_3^-} = \frac{P_{\text{H}_2\text{S}}}{P_{\text{CO}_2}} \quad (3.41)$$

This equation can be used to calculate the bisulfide ion (HS⁻) concentration. It can then be subtracted from the alkalinity to obtain the bicarbonate ion concentration for use in calculating the calcium carbonate saturation index.

Estimation of the Amount of CaCO₃ Scale Formed

It is possible to estimate the maximum amount of scale which could form, assuming that the system is at equilibrium.

If a solution is supersaturated with a salt (such as CaCO₃, CaSO₄, BaSO₄ or SrSO₄), precipitation can be expected. In this case, let us consider the general case of the formation of a mineral scale, MA. The general reaction is given as:



Assume that we have a solution that is supersaturated with respect to MA:

$$m \times a > K_c$$

Where:

- m = Initial concentration of M⁺⁺, moles/liter
- a = Initial concentration of A⁻, moles/liter
- K_c = Molar ion product constant

If the solution is allowed to reach equilibrium, MA will precipitate until the solution is saturated with MA. Since one mole of M⁺⁺ and one mole of A⁻ is required to make one mole of MA, the concentrations of both ions will be decreased by one mole for each mole of scale which precipitates.

Let P equal the number of moles of MA which precipitate in the act of reaching saturation.

Now:

$$K_c = (m - P)(a - P)$$

Rearranging:

$$P^2 - (m + a)P + ma - K_c = 0$$

Taking the negative root of the resulting quadratic equation:

$$P = \frac{m + a - \sqrt{(m - a)^2 + 4K_c}}{2}$$

Let: $G = m + a$, and
 $X = m - a$

Then:

$$P = \frac{G - \sqrt{X^2 + 4K_c}}{2}, \text{ moles/L}$$

Given the following relationship:

$$\text{mg/L} = \text{moles/L} \times \text{MW} \times 1000$$

Then:

$$P = 500 \times \text{MW} \times \left[G - \sqrt{X^2 + 4K_c} \right], \text{ mg/L} \quad (3.42)$$

Where: P = Maximum amount of scale which can precipitate, mg/L
 MW = Molecular weight of scale compound

This equation can be used to calculate the maximum amount of any scale which might precipitate.

Stiff & Davis

In order to solve this equation for the maximum amount of CaCO_3 which could precipitate using data from the Stiff and Davis SI calculation, the following substitution is required for the value of K_c as pointed out by Valone and Skillern:^(3.27)

$$K_c = 10^{k-\text{pH}} \quad (3.43)$$

Where: k = Stiff & Davis "k"
 pH = Actual system pH

Thus, for CaCO_3 , Equation 3.42 becomes:

$$P = 50000 \left[G - \sqrt{X^2 + 4 \times 10^{k-\text{pH}}} \right], \text{ mg/L} \quad (3.44)$$

In certain cases, it may be desirable to express the results in lb/1000 bbl.

$$\text{PTB} = \frac{\text{lb}}{1000 \text{ bbl}} = 0.35 \times \frac{\text{mg}}{\text{L}} \quad (3.45)$$

And Equation 3.24 becomes:

$$\text{PTB} = 17500 \left[G - \sqrt{X^2 + 4 \times 10^{k-\text{pH}}} \right] \quad (3.46)$$

Where: $G = \text{Ca}^{++} + \text{HCO}_3^-$, moles/L
 $X = \text{Ca}^{++} - \text{HCO}_3^-$, moles/L

Valone and Skillern^(3.27) further state that based on Texaco's experience, Table 3.5 can be used to assess the anticipated severity of calcium carbonate scale deposition.

TABLE 3.5
Calcium Carbonate Scaling Severity

PTB Value	Description
PTB < 0	No scale
0 < PTB < 100	Few scaling problems
100 < PTB < 250	Moderate scaling difficulties
PTB > 250	Severe scaling occurs

Oddo & Tomson

In the case of Oddo and Tomson, Equation 3.47 can be utilized to calculate K_c .

$$K_c = \frac{1}{10^{pK_c}} \quad (3.47)$$

Where:

$$pK_c = pH - 2.76 + 9.88 \times 10^{-3} T + 0.61 \times 10^{-6} T^2 - 3.03 \times 10^{-5} P - 2.348\sqrt{\mu} + 0.77\mu \quad (3.48)$$

The pH value in Equation 3.48 can be measured or calculated. Substituting into Equation 3.42 we obtain:

$$P = 50000 \left[G - \sqrt{X^2 + \frac{4}{10^{pK_c}}} \right] \quad (3.49)$$

Or when expressed in PTB:

$$PTB = 17500 \left[G - \sqrt{X^2 + \frac{4}{10^{pK_c}}} \right] \quad (3.50)$$

Sulfate Scaling Calculations

Traditional Approach to Sulfate Scale Solubilities

Solubility values for CaSO_4 , BaSO_4 or SrSO_4 , can be calculated using the following equation, providing values of conditional solubility product, K_c , are known for each compound:

$$\text{Solubility (meq/L)} = 1000 \left[\sqrt{X^2 + 4K_c} - X \right] \quad (3.51)$$

The derivation of this equation follows.

The Common Ion Effect

The maximum solubility of a slightly soluble salt is obtained when the concentrations of the cation and anion are equal.

For example: Given a saturated solution of CaSO_4 in water, where the Ca^{++} and $\text{SO}_4^{=}$ concentrations are equal:

$$\text{Ca}^{++} \text{ concentration} = S \text{ moles/liter}$$

$$\text{SO}_4^{=} \text{ concentration} = S \text{ moles/liter}$$

$$K_c = S \times S = S^2$$

$$S = \sqrt{K_c} \quad (3.52)$$

The solubility of calcium sulfate is equal to S moles/liter, which is simply the square root of the molar ion product constant.

However, in most natural waters, the cation and anion concentrations are not equal. In this case, the difference between the two concentrations is called the *excess common ion concentration*. The presence of excess common ion reduces the solubility of the salt unless a complex ion or ion pair, such as neutral magnesium sulfate, forms and offsets the effect.^(3.6)

For example, consider a saturated solution of CaSO_4 in water, where the Ca^{++} and $\text{SO}_4^{=}$ concentrations are unequal:

$$\text{Ca}^{++} \text{ concentration} = S \text{ moles/liter}$$

$$\text{SO}_4^{=} \text{ concentration} = S + X \text{ moles/liter}$$

In this case, we have arbitrarily selected the sulfate ion concentration as the larger of the two. The amount by which the sulfate ion concentration exceeds the calcium concentration, X , is the excess common ion concentration.

$$K_c = (S)(S + X) = S^2 + SX$$

The calcium sulfate solubility is equal to S moles/liter, since that is the maximum amount of calcium sulfate which can be formed by combining S moles of Ca^{++} with $(S + X)$ moles of $\text{SO}_4^{=}$.

Rearranging:

$$S^2 + SX - K_c = 0$$

Taking the positive root of the quadratic equation:

$$S = \frac{-X + \sqrt{X^2 + 4K_c}}{2}$$

For a divalent ion such as Ca^{++} , Ba^{++} or Sr^{++} :

$$S(\text{equivalents/L}) = \sqrt{X^2 + 4K_c} - X \quad (3.53)$$

Or:

$$S(\text{meq/L}) = 1000 \left[\sqrt{X^2 + 4K_c} - X \right] \quad (3.54)$$

The "actual concentration" of CaSO_4 in solution is equal to the smaller of the Ca^{++} or $\text{SO}_4^{=}$ concentrations (expressed in meq/liter) in the water of interest, since the smaller concentration controls the amount of calcium sulfate which can be formed.

The calculated calcium sulfate solubility, S (meq/liter), is compared with the actual concentration to determine if scale formation is likely.

TABLE 3.6
Interpretation of Sulfate Scale Calculations

Case	Conclusion
$S = \text{Actual}$	The water is saturated with CaSO_4 .
$S > \text{Actual}$	The water is undersaturated with CaSO_4 . Scale is unlikely.
$S < \text{Actual}$	The water is supersaturated with CaSO_4 . Scale is likely.

This formula can be used to calculate the solubility of any divalent salt such as CaSO_4 , BaSO_4 , or SrSO_4 .

Calcium Sulfate (Gypsum) Solubility Calculations

The data measured by Skillman, McDonald and Stiff^(3.28) has been widely used to estimate the solubility of gypsum in oilfield brines. They measured ion product constants in simulated oilfield brines over the following range:

- Temperature: 50, 95, 122 and 176°F [10, 35, 50 and 80°C]
- Ionic Strength: 0-6.0 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

Their data are presented in Appendix 15.

The following procedure is recommended to assess the possibility of gypsum precipitation from a given brine:

1. Calculate the molar ionic strength using Equation 3.38.
2. Obtain the appropriate value of K_c for the temperature of interest from Appendix 15.
3. Determine the excess common ion concentration, X , in moles/liter. This is simply the difference between the calcium concentration and the sulfate concentration.
4. Calculate the solubility of gypsum in meq/liter by solving Equation 3.54.
5. Calculate the "actual concentration" of gypsum in the water, which is equal to the smaller of the Ca^{++} or $\text{SO}_4^{=}$ concentrations expressed in meq/liter.
6. Compare the calculated solubility with the actual concentration to determine if precipitation of gypsum is likely.

An example calculation is given in Appendix 14.

Other commonly used methods for predicting calcium sulfate solubility which will not be presented here include those of Metler and Ostroff^(3.29), and Carlberg and Matthews.^(3.6) The latter method can be used for temperatures up to 257°F [125°C]. It assumes hemihydrate solubility to be the limiting solubility above 212°F [100°C].

Barium Solubility Sulfate Calculations

It is possible to estimate the solubility of barium sulfate for waters which contain predominately sodium and chloride ions and very little magnesium or calcium ions using the solubility data measured

by Templeton^(3.10) for sodium chloride solutions. Molar conditional solubility product constants calculated from his data are presented in Appendix 16 over the following range:

- Temperature: 77, 95, 122, 149, 176 and 203°F [25, 35, 50, 65, 80 and 95°C]
- Ionic Strength: 0-4.15 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

The solubility can be calculated using Equation 3.54, and the probability of BaSO₄ precipitation evaluated using the same procedure as previously outlined for gypsum.

Because BaSO₄ has such limited solubility, the appearance of Ba⁺⁺ and SO₄⁼ ions in any water indicates a danger of scale formation.

Strontium Sulfate Solubility Calculations

The solubility of strontium sulfate in sodium chloride solutions can be calculated in the same manner as the solubilities of the other sulfate scales.

Values of K_c have been measured by several investigators.^(3.12-3.15) However, the values measured by Jacques and Bourland^(3.13) cover the widest range of conditions thus published, and include the effect of pressure. The following equation is based on their data and can be used to estimate values of K_c:

$$\log K_c = \frac{X}{R} \quad (3.55)$$

Where: K_c = Conditional solubility product constant, molar units
X = 1/T

$$R = A + BX + C\sqrt{\mu} + D\mu + EP^2 + FXP + G\sqrt{\mu P} \quad (3.56)$$

The units are:

T = °K = °C + 273
P = Total pressure, psig
μ = Ionic strength, moles/L

The coefficients of the equation are:

A = 0.266498 × 10 ⁻³	E = -1.383 × 10 ⁻¹²
B = -244.828 × 10 ⁻³	F = 1.103323 × 10 ⁻⁶
C = -0.191065 × 10 ⁻³	G = -0.509 × 10 ⁻⁹
D = 53.543 × 10 ⁻⁶	

This equation applies over the following range:

- Temperature: 100-300°F [38-149°C]
- Ionic Strength: 0-3.45 moles/L
- Pressure: 100-3000 psig

K_c values measured by Fletcher, French and Collins^(3.14) for strontium sulfate in sodium chloride solutions at atmospheric pressure are given in Appendix 17. Their data was measured over the following range:

- Temperature: 50, 75, 122 and 156°F [10, 35, 50 and 69°C]
- Ionic Strength: 0.1-5.25 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

The Effect of Ion Pairing on Sulfate Scale Solubility

The sulfate ion will form neutral ion pairs or complexes with magnesium, calcium, barium and strontium ions. The fraction of these ions which are tied up as ion pairs depends on the temperature, pressure, ionic strength, and total concentrations of the ions in the solution.

The importance of ion pairing in scale prediction centers on the fact that ions occupied in ion pairs are not available to form scale.

For maximum accuracy, the available or “free” sulfate ion concentration should be used in sulfate scaling calculations. It can be calculated using the method of Oddo and Tomson presented in a following section.

Estimation of the Amount of Sulfate Scale Precipitated

When Equation 3.16 is used to calculate the solubility of the sulfate scales, the following equation can be used to calculate the maximum amount of scale which can precipitate:

$$P = (EW)(Actual - S) \quad (3.57)$$

Where:

- P = Maximum amount of scale which can precipitate (mg/L)
- EW = Gram equivalent weight of compound which precipitates
- Actual = Actual concentration of compound in solution, meq/L
- S = Calculated solubility of compound, meq/L

Oddo & Tomson Sulfate Scale Calculations — 1994^(3.4)

The equations published by Oddo and Tomson in 1994 permit the calculation of the Saturation Index, I_s , for five sulfate scales: Calcium sulfate (gypsum, hemi-hydrate, anhydrite), barium sulfate and strontium sulfate. The equations account for pressure, temperature, ionic strength and ion pairing.

Saturation index calculations have traditionally been reserved for calcium carbonate scale. The saturation index is defined in Equation 3.16.

Although Oddo and Tomson designated the saturation index as “ I_s ”, we have chosen to refer to it as SI in this book and to identify the particular sulfate scale compound with appropriate subscripts.

Mass Action Stability Constant

The degree of ion pairing can be predicted if the mass action stability constant, K_{st} , is known for each ion pair. In the case of the calcium and sulfate ions, the equation is given as:

$$K_{st} = \frac{[CaSO_4^o]}{[Ca^{++}][SO_4^{--}]} \quad (3.58)$$

Where: $[CaSO_4^o]$ = concentration of ion pair, moles/L
 $[Ca^{++}]$ = concentration of "free" calcium, moles/L
 $[SO_4^{--}]$ = concentration of "free" sulfate, moles/L

It is assumed that K_{st} values for the four sulfate/metal ion complexes are equal.

Free Ion Concentrations

The total concentration of a given ion in solution is measured in a water analysis. It is the sum of the paired ions and the "free" ions. Only the free ions are available to form scale.

In the case of sulfate, a material balance can be expressed as follows:

$$\underset{\text{Measured Concentration}}{C_{SO_4}} = \underbrace{[CaSO_4^o] + [MgSO_4^o] + [SrSO_4^o] + [BaSO_4^o]}_{\text{Paired Sulfate}} + \underbrace{[SO_4^{--}]}_{\text{Free Sulfate}} \quad (3.59)$$

Similar equations can be written for magnesium, calcium, barium and strontium ions.

$$\begin{aligned} C_{Ca} &= [Ca^{++}] + [CaSO_4^o] & C_{Mg} &= [Mg^{++}] + [MgSO_4^o] \\ C_{Sr} &= [Sr^{++}] + [SrSO_4^o] & C_{Ba} &= [Ba^{++}] + [BaSO_4^o] \end{aligned} \quad (3.60)$$

Sulfate Scale Calculations

1. Calculate the molar ionic strength.

$$\begin{aligned} \mu(\text{moles/L}) &= 10^{-5} (2.2 \times Na^+ + 5.0 \times Ca^{++} + 8.2 \times Mg^{++} + 1.5 \times Ba^{++} + 2.3 \times Sr^{++} \\ &\quad + 1.4 \times Cl^- + 2.1 \times SO_4^{--} + 0.8 \times HCO_3^-) \end{aligned} \quad (3.61)$$

Where all ion concentrations are in mg/L and are obtained from a water analysis.

2. Calculate K_{st}

$$K_{st} = 10^{\log K_{st}} \quad (3.62)$$

Where:

$$\log K_{st} = +1.86 + 4.5 \times 10^{-3} T - 1.2 \times 10^{-6} T^2 + 10.7 \times 10^{-5} P - 2.38 \sqrt{\mu} + 0.58 \mu - 1.3 \times 10^{-3} \sqrt{\mu} T \quad (3.63)$$

and: T = Temperature ($^{\circ}\text{F}$)
 P = Total Pressure (psia)
 μ = Ionic Strength (moles/L)

3. Convert the ion concentrations from mg/L to moles/L by dividing the ion concentrations obtained from the water analysis by the appropriate conversion factor given in Table 3.7.

TABLE 3.7

Conversion Factors: mg/L to moles/L

Ion Concentration (mg/L) From Water Analysis	Divide by	To Obtain Total Concentration (moles/L)
$\text{SO}_4^{=}$	96060	C_{SO_4}
Ca^{++}	40080	C_{Ca}
Mg^{++}	24305	C_{Mg}
Sr^{++}	87620	C_{Sr}
Ba^{++}	137330	C_{Ba}

4. Calculate CatSum. This is the sum of the four measured metal cation concentrations (moles/L).

$$\text{CatSum} = C_{\text{Ca}} + C_{\text{Mg}} + C_{\text{Sr}} + C_{\text{Ba}} \quad (3.64)$$

5. Calculate the free sulfate concentration (moles/L).

$$[\text{SO}_4^{=}] = \frac{-\left\{1 + K_{st}(\text{CatSum} - C_{\text{SO}_4})\right\} + \left\{\left[1 + K_{st}(\text{CatSum} - C_{\text{SO}_4})\right]^2 + 4K_{st}C_{\text{SO}_4}\right\}^{0.5}}{2K_{st}} \quad (3.65)$$

6. Calculate the free metal-ion concentrations.

$$\begin{aligned} [\text{Mg}^{++}] &= \frac{C_{\text{Mg}}}{1 + K_{st}[\text{SO}_4^{=}]} & [\text{Ca}^{++}] &= \frac{C_{\text{Ca}}}{1 + K_{st}[\text{SO}_4^{=}]} \\ [\text{Sr}^{++}] &= \frac{C_{\text{Sr}}}{1 + K_{st}[\text{SO}_4^{=}]} & [\text{Ba}^{++}] &= \frac{C_{\text{Ba}}}{1 + K_{st}[\text{SO}_4^{=}]} \end{aligned} \quad (3.66)$$

7. Calculate the Saturation Index values for the sulfate scales.

Calcium Sulfate

Equations are given for the calculation of the Saturation Index (SI) for three forms of calcium sulfate scale: gypsum, hemi-hydrate and anhydrite. According to Oddo and Tomson, the most likely scale to form from brines will be gypsum at temperatures less than 176°F [80°C].

Between 176°F [80°C] and 250°F [121°C], any of the three types of calcium sulfate may form, with gypsum being more likely at the low end of the temperature range and anhydrite more likely at the high end. Hemihydrate is commonly found in this temperature range in non-turbulent systems with high ionic strengths.

Above 250°F [121°C], any calcium sulfate scale formed will almost certainly be anhydrite.^(3,4)

The saturation index for the three forms of calcium sulfate follow.

- Gypsum

$$SI_{Gyp} = \log_{10} \{ [Ca^{++}] [SO_4^{--}] \} + 3.47 + 1.8 \times 10^{-3} T + 2.5 \times 10^{-6} T^2 - 5.9 \times 10^{-5} P - 1.13 \sqrt{\mu} + 0.37 \mu - 2.0 \times 10^{-3} \sqrt{\mu} T \quad (3.67)$$

- Hemi-hydrate

$$SI_{Hemi} = \log_{10} \{ [Ca^{++}] [SO_4^{--}] \} + 4.04 - 1.9 \times 10^{-3} T + 11.9 \times 10^{-6} T^2 - 6.9 \times 10^{-5} P - 1.66 \sqrt{\mu} + 0.49 \mu - 0.66 \times 10^{-3} \sqrt{\mu} T \quad (3.68)$$

- Anhydrite

$$SI_{Anhy} = \log_{10} \{ [Ca^{++}] [SO_4^{--}] \} + 2.52 + 9.98 \times 10^{-3} T - 0.97 \times 10^{-6} T^2 - 3.07 \times 10^{-5} P - 1.09 \sqrt{\mu} + 0.50 \mu - 3.3 \times 10^{-3} \sqrt{\mu} T \quad (3.69)$$

Barium Sulfate

$$SI_{Ba} = \log_{10} \{ [Ba^{++}] [SO_4^{--}] \} + 10.03 - 4.8 \times 10^{-3} T + 11.4 \times 10^{-6} T^2 - 4.8 \times 10^{-5} P - 2.62 \sqrt{\mu} + 0.89 \mu - 2.0 \times 10^{-3} \sqrt{\mu} T \quad (3.70)$$

Strontium Sulfate

$$SI_{Sr} = \log_{10} \{ [Sr^{++}] [SO_4^{--}] \} + 6.11 + 2.0 \times 10^{-3} T + 6.4 \times 10^{-6} T^2 - 4.6 \times 10^{-5} P - 1.89 \sqrt{\mu} + 0.67 \mu - 1.9 \times 10^{-3} \sqrt{\mu} T \quad (3.71)$$

MIXING WATERS — COMPATIBILITY

One of the primary causes of scale formation and injection well plugging is mixing two or more waters which are incompatible. The individual waters may be quite stable at all system conditions and present no scale problems. However, once they are mixed, reactions between ions dissolved in the individual waters may form insoluble products. When this occurs, the waters are said to be incompatible.

For example, it would be a mistake to mix a water which contained a large quantity of barium (Ba^{++}) with a water containing a large amount of sulfate ($\text{SO}_4^{=}$); the formation of BaSO_4 would be almost certain.

Two waters might be described qualitatively as shown in Table 3.8:

Table 3.8
Two Qualitative Water Analyses

Component	Water "A"	Water "B"
Ca^{++}	Present	Absent
HCO_3^-	Absent	Present
$\text{SO}_4^{=}$	Absent	Present
Ba^{++}	Present	Absent
Fe^{++} or Fe^{+++}	Absent	Present
H_2S	Present	Absent

Depending on the amounts of each constituent present, the pH, temperature and the ratio in which the two waters are mixed, you might expect any or all of the following precipitates to result: calcium carbonate, calcium sulfate, barium sulfate or iron sulfides.

The situation is further complicated if more than two waters are mixed.

Mixing two or more incompatible waters on the surface for subsurface injection is obviously undesirable.

Incompatibility Between Injection and Formation Waters

The second area where problems may arise from incompatibility is when the injection water is not compatible with the natural formation water (connate water) in the zone where the water is being injected. Surprisingly, very few plugging problems due to incompatibility occur in the injection well.

When water is injected into a well, the injection water miscibly displaces the connate water. Mechanical mixing occurs at the boundary between the two liquids. This mixing phenomenon is called *hydrodynamic dispersion*. Non-homogeneous permeability distribution has been suggested as the primary cause of dispersion. In addition, dissolved ions migrate across the boundary between the two waters as a result of *diffusion*.

The relative contributions of hydrodynamic dispersion and ionic diffusion to the total mixing process are a function of the velocity with which the boundary between the two waters moves through the reservoir rock. In most injection operations, the injection rates are such that dispersion is the predominate cause of mixing. However, in most laboratory studies, the individual contributions of dispersion and diffusion are not separated, and the amount of mixing is described by an apparent coefficient of dispersion, which includes both effects.

Warner^(3.30) gives equations for the width and volume of the mixing zone:

$$w = 4.619\sqrt{D' r} \quad (3.72)$$

$$V_m = 5.17h\phi\sqrt{D' r^3} \quad (3.73)$$

Where: w = Width of mixing zone, ft
 V_m = Volume of mixing zone, bbl
 D' = D/v = Coefficient of dispersion, ft
 D = Coefficient of dispersion, ft²/sec
 v = Average velocity of fluid flow, ft/sec
 r = Radial distance from the wellbore to the center of the mixing zone, ft
 h = Thickness of injection zone, ft
 ϕ = Porosity of reservoir rock, expressed as a fraction

Figure 3.16 illustrates the growth of the mixing zone as it moves away from the injection wellbore.

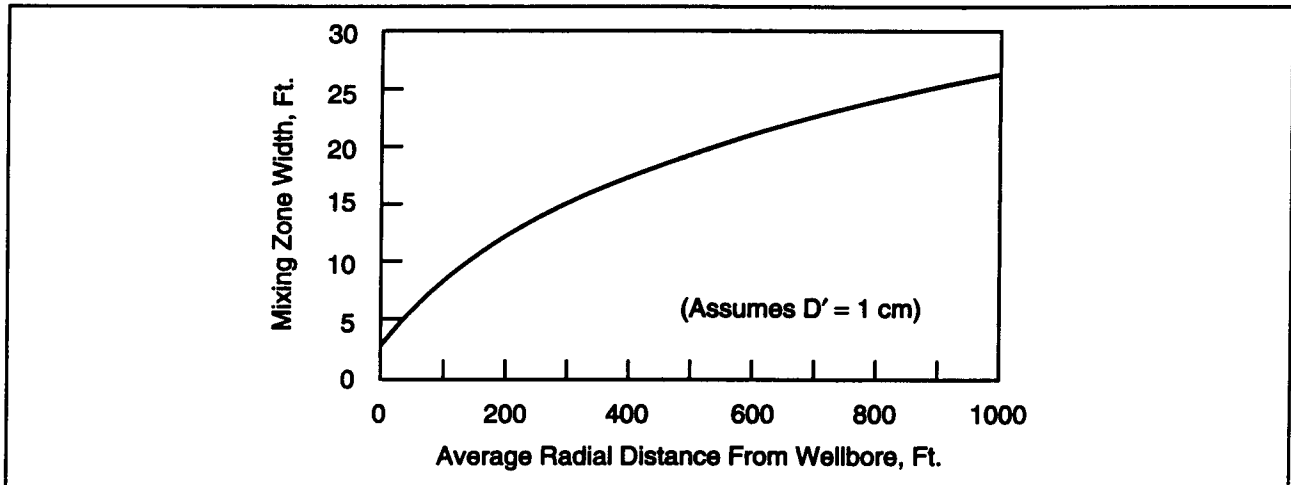


Figure 3.16 Mixing Zone Width as a Function of Distance

The radial distance from the injection wellbore to the center of the mixing zone is given as follows:

$$r = \sqrt{1.79 \frac{V_i}{h\phi}} \quad (3.74)$$

Where: V_i = Volume of water injected, bbl

The radial distance to the leading edge of the mixing zone from the wellbore is equal to $r + 0.5 w$. Therefore, the total cumulative pore volume which is contacted by the mixing zone from the time it leaves the wellbore until it reaches a radius, r , is:

$$V_c = 0.56h\phi(r + 0.5w)^2 \quad (3.75)$$

Where: V_c = Volume of pore space contacted by leading edge of mixing zone, bbl

If one assumes the worst case, that two waters are completely mixed within the mixing zone (which they are not), it is possible to calculate the maximum volume of scale which could precipitate for a given set of conditions.

$$V_p = 2.9 \times 10^{-6} \frac{V_m PPT}{SG} \quad (3.76)$$

Where: V_p = Volume of scale precipitated, bbl
PPT = Weight of scale precipitated, lb/1000 bbl
SG = Specific gravity of the scale formed

Example

Assume the following:

1. The two waters are completely mixed within the mixing zone.
2. Barium sulfate is being formed in the mixing zone. The specific gravity of BaSO_4 is 4.2.
3. The maximum amount of scale which can precipitate is 100 mg/L (35 lb/1000 bbl).
4. The injection zone is 10 ft thick.
5. The fractional porosity of the injection zone is 0.20.
6. $D' = 1.0 \text{ cm} = 0.033 \text{ ft}$.

It is now possible to calculate the mixing zone volume, the total volume of reservoir pore space contacted, and the volume of precipitate formed, as a function of the volume of water injected. The results for the conditions stated in the example are presented in the Table 3.9.

The precipitate thus formed is distributed throughout the total volume of pore space contacted by the mixing zone, V_c , and occupies a negligible fraction of that space. In addition, once the mixing zone has passed a given point in the reservoir, any precipitate is exposed solely to the injection water, and will often be at least partially redissolved.^(3.30) Therefore, one would not anticipate any significant reduction in injectivity due to incompatibility.

Several investigators have reported laboratory experiments which confirm this conclusion, both in rocks containing 100% water^(3.30,3.31) and where an oil saturation is present.^(3.31) Injection well plugging due to this phenomena is considered extremely unlikely.

If you wish to avoid completely any possibility of permeability reduction, it is possible to inject a buffer zone of a third water which is mutually compatible with both the injection water and the connate water. The volume required to totally eliminate mixing to any given radius is equal to the volume of the mixing zone, V_m , and can be calculated from Equation 3.73.

It is also possible to treat the injection water with a scale preventive chemical to prevent precipitation in the immediate area of the injection wellbore. However, this approach is unlikely to be effective farther out in the reservoir since most scale inhibitors have a strong tendency to adsorb on solid surfaces. The large amount of surface area presented by the reservoir rock makes it extremely likely that all inhibitor will be adsorbed by the rock within a very short distance from the wellbore.

So the good news is that injection well plugging due to incompatibility between the injection water and the connate water is an extremely unlikely event.

However, there is some accompanying bad news: Severe scale formation can occur in the producing wells after injection-water breakthrough.

TABLE 3.9
Reservoir Mixing Calculations

<i>Volume</i> V _i (bbl)	r (ft)	W (ft)	<i>Mixing zone</i> V _m (bbl)	<i>Injection</i> V _c (bbl)	<i>Producer</i> V _p (bbl)
1	1	0.8	2	2	4.1×10^{-5}
10	3	1.5	10	15	2.3×10^{-4}
10 ²	9	2.6	54	126	1.3×10^{-3}
10 ³	30	4.6	306	1151	7.3×10^{-3}
10 ⁴	95	8.1	1733	10833	4.1×10^{-2}
10 ⁵	299	14.5	9675	104736	2.3×10^{-1}
10 ⁶	945	25.7	54364	1027617	1.29

This can occur because there is ample opportunity for mixing of large volumes of injection water and connate water in the producing wells after breakthrough of injection water. When the producing zone is comprised of several layers of different permeability (which is usually the case), the injection water will break through earlier in some layers than in others. The result is the simultaneous production of both injection and connate water. Simultaneous production of both waters can also occur due to differing breakthrough times for water from several injectors into a single producer.

Even in relatively homogeneous reservoirs, simultaneous production of the two waters will occur since the reservoir volume swept by the injection water increases with time. Both injection water from the swept area and connate water from the unswept area will enter the producing wellbore, and the relative amounts will change over the life of the flood.

Evaluation of Incompatibility

Compatibility of water mixtures is assessed either by solubility calculations or by experimental testing.

Solubility Calculations

If solubility calculations are to be performed, the following procedure is recommended:

1. Obtain analyses of the waters to be mixed.
2. Calculate a composite analysis for the waters at various mixing ratios of interest.
3. Calculate the average pH values for the various mixtures
4. Calculate the scaling tendencies of the mixtures.

Calculating the pH of a Mixture

$$pH = -\log[H^+]; \text{ therefore, } [H^+] = 10^{-pH} \quad (3.77)$$

$$pH_{avg} = -\log\{F_1[H^+]_1 + F_2[H^+]_2 + F_3[H^+]_3 + \dots + F_n[H^+]_n\} \quad (3.78)$$

Where: $[H^+]$ = Hydrogen ion concentration, moles/liter

$F_1, F_2, F_3, \dots, F_n$ = Fraction of each water in a given mixture

$[H^+]_1, [H^+]_2, [H^+]_3, \dots, [H^+]_n$ = Hydrogen ion concentration of each water

Compatibility Testing

Fresh samples of the waters to be mixed are taken, filtered to remove any suspended solids and then mixed in several ratios. The various sample mixtures are set aside and observed to see if any precipitation occurs.

This procedure is quite useful for the detection of potential calcium, barium, or strontium sulfate precipitation problems. However, it cannot be relied upon to give an accurate indication of the precipitation of calcium carbonate or iron compounds because both are quite sensitive to pH changes. The solubility of sulfate compounds is largely insensitive to changes in pH.

PREVENTING SCALE FORMATION

Avoid Mixing Incompatible Waters

The importance of staying away from compatibility problems should be obvious from the preceding discussion. Always be extremely careful when you are considering mixing waters.

If you have two incompatible waters on the surface, and you wish to inject them both, there are two methods of doing so without incompatibility problems.

1. Split System

Inject the two waters through separate injection systems into two different groups of wells.

2. Sequential Injection

Store the two waters in two sets of tanks and inject them alternately. The zone of mixing in the injection line is small, and the volume of precipitate generated is insufficient to cause plugging in the injection wells.

Water Dilution

This is just the reverse of the preceding problem. An injection water that normally would be scale forming may be diluted with another water so that the resulting mixture is stable at system conditions.

pH Control

Lowering the pH will increase the solubility of iron compounds and carbonate scales. However, it will also tend to make the water more corrosive, and may create corrosion problems. pH has little, if any, effect on the solubility of sulfate scales.

This is not a widely used method of scale control. It is usually practical only if a small shift in pH is necessary to prevent precipitation of insoluble compounds. Accurate pH control is also necessary and this is often difficult in normal oilfield operations.

Removal of Scale Forming Constituents

Dissolved Gas Removal

Dissolved gases such as H_2S , CO_2 , and O_2 can be removed from the water by chemical and/or mechanical means. This can eliminate the formation of insoluble iron compounds.

Simply removing CO_2 from water will actually increase the severity of scale deposition. However, the pH can be lowered sufficiently to convert all carbonates and bicarbonates to CO_2 . Then removal of CO_2 will prevent the formation of carbonate scales.

Dissolved gas removal is discussed in Chapter 6.

Water Softening

Processes such as ion-exchange, precipitation softening or distillation are seldom used to prevent scale deposition from injection waters. These processes remove scale forming cations such as Ca^{++} and Mg^{++} and may be used alone or in combination.

The problem with using these processes with oilfield brines centers on the cost involved to remove the inherently large quantities involved. It is nearly always far cheaper to use other methods of scale control.

Of the processes listed, ion-exchange is probably the most generally applied in oilfield-related operations. Ion-exchange units have been widely used to soften water for use as boiler feed water in gas processing plants and for steam generators used in thermal recovery operations. They also are used to soften water in several of the enhanced oil recovery processes.

Ion exchange and other ion removal processes are discussed in Chapter 6.

Nanofiltration

Nanofiltration membranes have been developed which selectively remove divalent ions such as sulfate, magnesium and calcium. Monovalent ions such as sodium and chloride pass through the membrane.

This technology has been applied in the North Sea to reduce the sulfate concentration of the injected seawater as a means of controlling barium sulfate scale formation in the producing wells resulting from incompatibility with the formation water.^(3.49) Sulfate removal efficiency is reported to be as high as 98% at a recovery of 75%.

A recovery of 75% means that 75% of the incoming water will be processed for injection. The remaining 25% is the concentrated reject stream which contains the ions removed from the injection water. It is discharged overboard.

Scale Control Chemicals

Scale inhibitors are chemicals which will delay, reduce or prevent scale formation when added in small amounts to a normally scaling water. Most of the scale inhibitors used in the oilfield function by one or both of the following mechanisms:

- When scales first begin to form, very tiny crystals precipitate from the water. At this point, the scale inhibitor *adsorbs* onto the surface of the crystals while they are still very tiny and prevents further growth. This is thought to be the primary mechanism by which most oilfield scale inhibitors work.
- In some cases scale inhibitors prevent the precipitated scale crystals from adhering to solid surfaces such as piping or vessels.

The mechanisms by which scale inhibitors accomplish one or both of these objectives are not completely understood.^(3.32)

It seems clear that a scale inhibitor which prevents precipitation is required for water injection operations. If precipitation occurs the scale particles can still form deposits and contribute to plugging even if they are prevented from forming adherent scales.

The fact that most commonly used scale inhibitors function by inhibiting the growth of the scale crystals means that the inhibitor must be present in the water at the point where the crystals begin to form. Providing an effective chemical has been chosen, two rules must be observed if scale inhibition is to be successful.

- The inhibitor must be present in the water at the point where scale crystals begin to form in order to have maximum effectiveness in inhibiting further growth. This means that the inhibitor must be applied upstream of the problem area.
- The inhibitor must be present in the water on a continuous basis so that it is available to inhibit the growth of each scale crystal as it precipitates from the water. Therefore, continuous injection of scale inhibitor is required.

All commonly used scale inhibitors are organic compounds. The most common types are:

- Phosphate Esters

Phosphate esters are not recommended for application above approximately 175°F [79°C] as there is a danger of hydrolysis (reaction with H₂O) resulting in a loss of effectiveness.

- Phosphonates

Phosphonates are more temperature stable than the esters and should provide some protection up to 350°F [175°C].

- Polymers

Polymers such as the acrylics are primarily used for high temperature applications. They can be used up to 350°F [175°C].

Selection and Evaluation of Scale Inhibitors

Like any other operation in the oilfield, scale inhibitors should be selected on a cost/effectiveness basis. It is very tempting to choose the cheapest chemical available. This is very often a tragic error. Sometime the most expensive material on a *cost per unit volume of chemical* basis will be the cheapest to use based on *cost per volume of water treated*.

1. Chemical Composition of the Scale

Certain compounds are more effective for specific scales.

2. Severity of Scaling

The efficiency of scale inhibitors is primarily dictated by the level of supersaturation. The higher the saturation index, the more difficult it is to inhibit scale formation.

3. System Temperature

Scale inhibitors generally become less effective as the temperature increases. Each inhibitor has an upper temperature limit above which they become progressively less effective.

4. Laboratory Scale Inhibitor Performance Tests

Laboratory scale inhibitor performance tests are comparative tests which determine percent inhibition as a function of scale inhibitor concentration. The data from this type of testing is intended to measure relative inhibitor effectiveness. It does not provide a recommended scale inhibitor treatment concentration for field use.

5. Effect of Suspended Solids

If substantial amounts of suspended solids are present, higher inhibitor concentrations will be necessary. The reason is that scale inhibitors will adsorb onto the surface of solids in the water, thereby reducing the amount available to inhibit scale formation.

6. Compatibility with Other Chemicals

The scale inhibitor should be compatible with any other chemicals being added to the system, such as oxygen scavengers, corrosion inhibitors, or biocides. It is important that there is no reaction or interference among the different chemicals being used in a system.

7. Compatibility with the Water

Some scale inhibitors will react with calcium, magnesium or barium ions to form rather insoluble compounds. Precipitation of these compounds can result in the formation of a scale, thus creating a new problem. Generally, phosphonates and polymers are more prone to give this problem than the esters.^(3,32)

If high concentrations of these ions are present in the water the scale inhibitor must be selected with care to avoid this problem.

8. Effect of Dissolved Iron on Calcium Sulfate Inhibition

Most scale inhibitors are less effective in inhibiting calcium sulfate scale formation when dissolved iron is present in the water. The effect is severe in the case of phosphate esters and phosphonates, while most polymers show only slight decreases in performance.

While it is possible to compensate for this effect by increasing the scale inhibitor concentration, the additional cost can be substantial.

Soluble iron concentrations are typically quite low in sour waters and in waters containing dissolved oxygen, since most of the iron will precipitate as iron sulfide or ferric hydroxide. However, concentrations can be substantial in sweet, air-free systems.

Since corrosion is the most common source of soluble iron in oilfield waters, an effective corrosion control program is essential for cost-effective scale inhibition. If the source of iron is the producing formation, the use of polymer-type scale inhibitors should be considered.

9. Effect of pH

Some scale inhibitors become less effective against BaSO_4 and CaSO_4 scales at pH values below 6. Since values less than 6 are quite common in oilfield waters, this can be an extremely important consideration in chemical selection.

10. Weather

Is it a cold weather operation? Be sure to determine the pour point of any scale inhibitors and design the chemical injection system to avoid freezing problems.

Inhibitor Application

Organic scale inhibitors are supplied as liquids with the exception of certain polymers which can be obtained in powder form. The powder is dissolved in water prior to application.

Organic inhibitors are applied to surface facilities and injection wells by continuous injection using standard chemical pumps. It is essential that pumps be maintained and checked frequently to ensure that the proper amount of chemical is being injected. This is especially important for scale

inhibitors since they must be injected on a continuous basis to be effective. Therefore, the success of any scale inhibition program will depend on the percentage of time which the pump is operating properly. If the chemical pump is down half of the time, the most effective scale inhibitor cannot be expected to give good results.

Scale problems in water-supply wells are treated by continuous injection from the surface or by squeezing the inhibitor into the water producing formation. The choice of methods usually depends on the well completion and the nature of the problem.

Monitoring

The minimum effective scale inhibitor concentration is often difficult to determine with precision. Some commonly used monitoring methods are:

- Pipe Spools or Nipples

Often used for corrosion monitoring, spools are simply short sections of pipe installed at various locations which may be removed and inspected for scale buildup. If scale is present, the thickness can be measured or the scale can be scraped off and weighed. In order to be useful, the spool must be easily removable from the system. In some cases it is relatively simple to depressure the system and remove the spool. In other cases the system cannot be easily depressured and a bypass around the spool should be installed so that operation can continue while the spool is being removed.

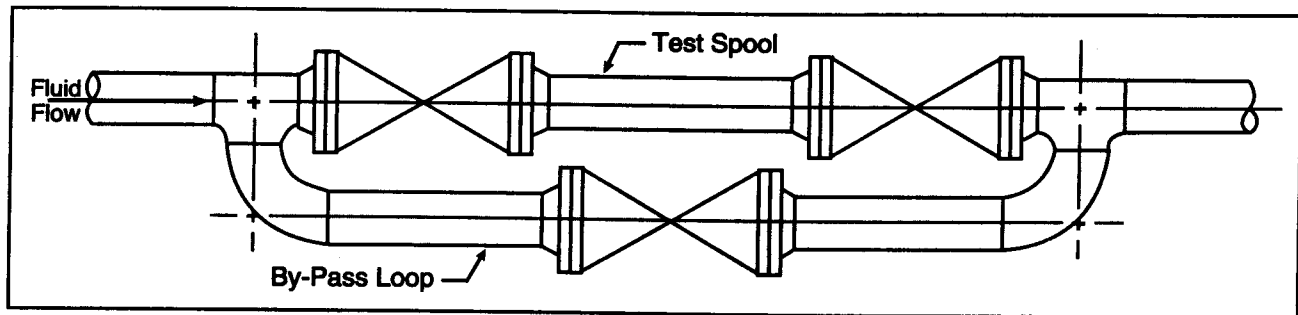


Figure 3.17 Pipe Spool Installed in Bypass Loop

- Scale Coupons

Scale coupons may be used to detect scale buildup. They are similar to corrosion coupons except that they are perforated with a minimum of 6 to 8 holes. The coupon is placed in the system with the flat side facing the direction of flow. This induces turbulence which accentuates any scaling tendencies. The coupon is weighed before and after exposure to the fluid and the amount of scale determined by the difference in the two weights.

- Visual Inspection

Although not too quantitative, this method is quite reliable. Look inside tanks, break open lines, look inside valves, look for spots where you might expect scale and inspect them *regularly*.

- Infrared Thermography

Infrared thermography has been used to detect and monitor internal scale accumulations in North Sea production facilities. This technique is used to measure the surface temperature of piping and vessels which handle hot produced fluids. Internal scale accumulations will

cause the external temperature to be cooler than normal due to the fact that scales have a lower thermal conductivity than steel.

- Increased Pressure Drops in the System

The flow rate must also be measured.

- Decreased Injectivity

Injectivity decline is evidenced by increasing injection pressures to maintain injection rate. This indicates formation plugging which may be due to scale particles. It also may be due to other causes.

Non-Chemical Scale Control Devices

Various devices are available which are claimed to prevent scale deposition. Water is passed through the device, and scale is prevented by rather vaguely described mechanisms. There are three major categories of devices:

Magnetic Treatment Devices

A magnetic field (imposed by either a permanent magnet or an electromagnet) is claimed to cause alterations in the structure of water or dissolved ions, which prevents scale formation.^(3.33-3.36)

Electrostatic Devices

They typically contain an electrically insulated, electrostatically charged electrode which is claimed to neutralize or alter the ionic charges, thus preventing scale.^(3.33)

Catalytic Devices

Pressure fluctuations within the device are said to cause precipitation on a special alloy metallic core which is washed away as a suspension of scale crystals.^(3.33)

Theories proposed to explain the operation of these devices are typically unsubstantiated and could charitably be described as pseudoscientific.^(3.35) Both positive and negative results have been reported for both laboratory and field application of the devices. However, the conditions under which the devices are evaluated are often poorly controlled and documented, leaving ample room for skepticism.

Based on presently available information, the use of any of these devices to prevent scale formation in oilfield systems cannot be recommended.

SCALE REMOVAL

Scale Identification

The success in removing scale accumulations will be determined to a great extent by your knowledge of the scale composition. Identify the problem correctly and you have a much greater probability of solving it.

We have already covered methods of predicting which types of scales might be expected for a particular water under certain conditions. However, the only reliable method of assessing the problem is to obtain a sample of the scale or plugging solids and analyze it.

If scale is occurring in surface facilities, a sample can be obtained by opening the system and scraping out some of the scale. Samples can be obtained from an injection well by backflowing the well or by running a bailer.

The general scheme for identifying the components of a scale sample is much the same whether performed in a commercial laboratory or in the field. The primary difference is that a laboratory analysis will usually give the amount of each component present, where a field analysis is very qualitative. A quantitative scale analysis procedure is given by Ostroff^(3.1).

Field Scale Analysis

In a field scale analysis we attempt to guess the composition of the solid by doing the following:

- Soak the sample in a solvent to dissolve any hydrocarbons. Watch to see if the solvent gets darker in color.
- Check to see if the sample is magnetic. If it is strongly magnetic, it probably contains a major amount of Fe_3O_4 (magnetic iron oxide). If it is weakly magnetic, it may contain a small amount of Fe_3O_4 , or it may be iron sulfide.
- Place the sample in 15% HCl. Note whether or not a violent reaction occurs. Note any smell. (H_2S indicates FeS .) Note the color of the acid. If it turns yellow, an iron compound is indicated.

It should be noted that when iron sulfide is placed in contact with air, it will oxidize and convert to an iron oxide. This means that the composition of scales or deposits originally containing iron sulfide is a function of the length of time the deposit has been exposed to air. Analyses performed several days or weeks after the sample has been removed from the system will frequently find predominantly iron oxide and little or no iron sulfide.

- Check the solubility in water. NaCl is water soluble.

Qualitative identification of the components present can be summarized in terms of the preceding properties in Table 3.10.

TABLE 3.10
Qualitative Analysis of Scales

Component	Soluble in Solvent	Soluble in HCl				Soluble in Water
		Magnetic	Reaction	Acid Color	Smell	
Hydrocarbon	Yes		Violent			
CaCO_3						
CaSO_4						
BaSO_4						
SrSO_4						
FeS		Weak	Strong	Yellow	Stinks!(H_2S)	
Fe_2O_3			Weak	Yellow		
Fe_3O_4		Strong	Weak	Yellow		
FeCO_3			Very strong	Yellow		
NaCl						
Sand, Silt, Clay						Yes

Note: Neither sulfates nor sand, silt or clay reacts with anything. A magnifying glass may help to recognize sand grains or spot sulfate crystals. However, if nothing happens to the sample when you run a field analysis, send a fresh sample (not the one you worked on) to a commercial laboratory.

After the sample has been identified a scheme to dissolve or remove the scale or deposit can be formulated. Chemical removal of scale follows the same principles as scale analysis. Basically, the problem is to find something that will dissolve the various components of the deposit. If it consists primarily of a single component, such as calcium carbonate, then a single solvent (hydrochloric acid in this case) is sufficient. If it contains more than one component, a series or combination of treating chemicals may be dictated. In addition, mechanical removal methods may be used, either alone or in conjunction with chemicals.

Scale Removal Chemicals

Hydrocarbons

Although hardly a scale, hydrocarbons are often present and can greatly interfere with the action of acid or other scale removal chemicals. Acid will not react with oil-coated scale! A hydrocarbon solvent is needed to remove any oil, paraffin or asphaltic materials on the scale so that the chemical of your choice can get at the solid scale.

Selection of a solvent for hydrocarbons is usually based on trial and error. However, we do know that the more asphaltic the oil or deposit, the more aromatic the solvent should be. The best approach is to consult your chemical supplier.

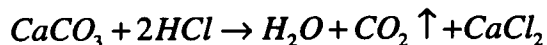
Hydrocarbon solvents can be applied as a pre-wash. They have also been emulsified in hydrochloric acid to improve its effectiveness.^(3.37)

In addition to simple organic and inorganic solvents, various complex proprietary solvents are available which can be used alone to remove oil^(3.38,3.39) or can be miscibly mixed with hydrochloric acid to improve its effectiveness in penetrating hydrocarbons.^(3.40) These materials range from mixtures of alcohols to micellar solutions.

Calcium Carbonate

Hydrochloric Acid

is recommended as the cheapest and easiest way to dissolve CaCO_3 scale under most conditions. Concentrations of 5, 10, or 15% HCl are normally used.



A corrosion inhibitor must be added to the acid to keep it from dissolving the pipe. You should think of the useful lifetime of an acid inhibitor in terms of hours rather than days or weeks. Once the inhibitor ceases to be effective, the pipe will be subject to extremely severe pitting which often results in perforation of the pipe wall. Therefore, it is essential that all acid be immediately flushed from the system once the cleanout is completed.

A surfactant is often added to help remove any oil film from the scale, but a pre-wash with a solvent or addition of one of the previously mentioned proprietary solvents is preferred unless the amount of oil is extremely small. Acid will either not react at all or it will react very slowly if the scale is oily.

Figure 3.18 shows the effect of a coating of light oil on the reaction rate of 10% HCl with CaCO₃ scale. The scale was 1/8" thick on the internal surface of a 1/4" x 1" nipple.

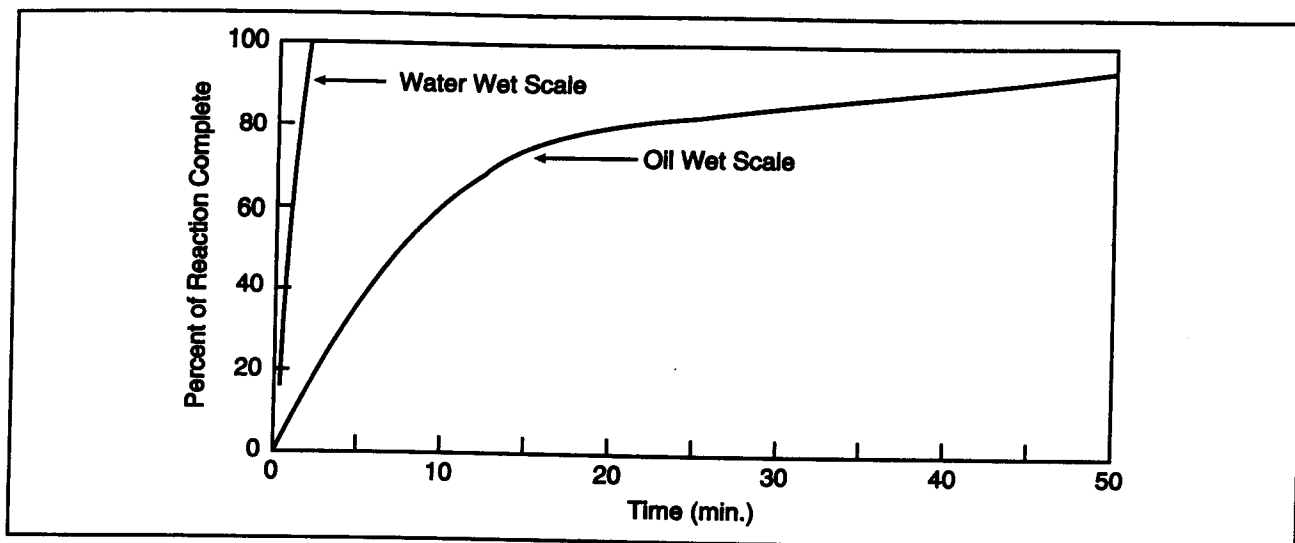


Figure 3.18 Reaction Rate of HCl with CaCO₃ Scale^(3.5)

Table 3.11 gives the amount of CaCO₃ which will be dissolved by different concentrations of HCl.

TABLE 3.11
Reaction of HCl with Calcium Carbonate

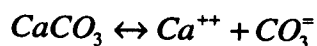
% HCl	CaCO ₃ Dissolved (lbs/gal of acid)
5	0.6
7.5	0.9
10	1.2
15	1.8
28	3.7

Figure 3.19 is helpful in calculating the amount of 15% HCl required to dissolve various acid soluble scales.

Chelating Agents

It is possible to dissolve calcium carbonate scale with chelating agents, such as EDTA (ethylenediaminetetraacetic acid). They function by reacting with the calcium ion to form a water soluble complex, thereby effectively removing the ion from solution.

When calcium carbonate scale is in equilibrium with a water which contains calcium ions and carbonate ions, then the equilibrium can be described as:



If a chelating agent is added to the water, some of the calcium ions will be chelated, resulting in a decrease in the Ca⁺⁺ ion concentration. When this occurs, some of the CaCO₃ scale will dissolve and replace the Ca⁺⁺ ions lost to the chelating agent in order to maintain the equilibrium of the reaction.

For $\begin{bmatrix} \text{CaCO}_3 \\ \text{Fe}_2\text{O}_3 \\ \text{FeS} \end{bmatrix}$ use $\begin{bmatrix} 95 \\ 318 \\ 180 \end{bmatrix}$ gal 15% HCl/ft³ of scale

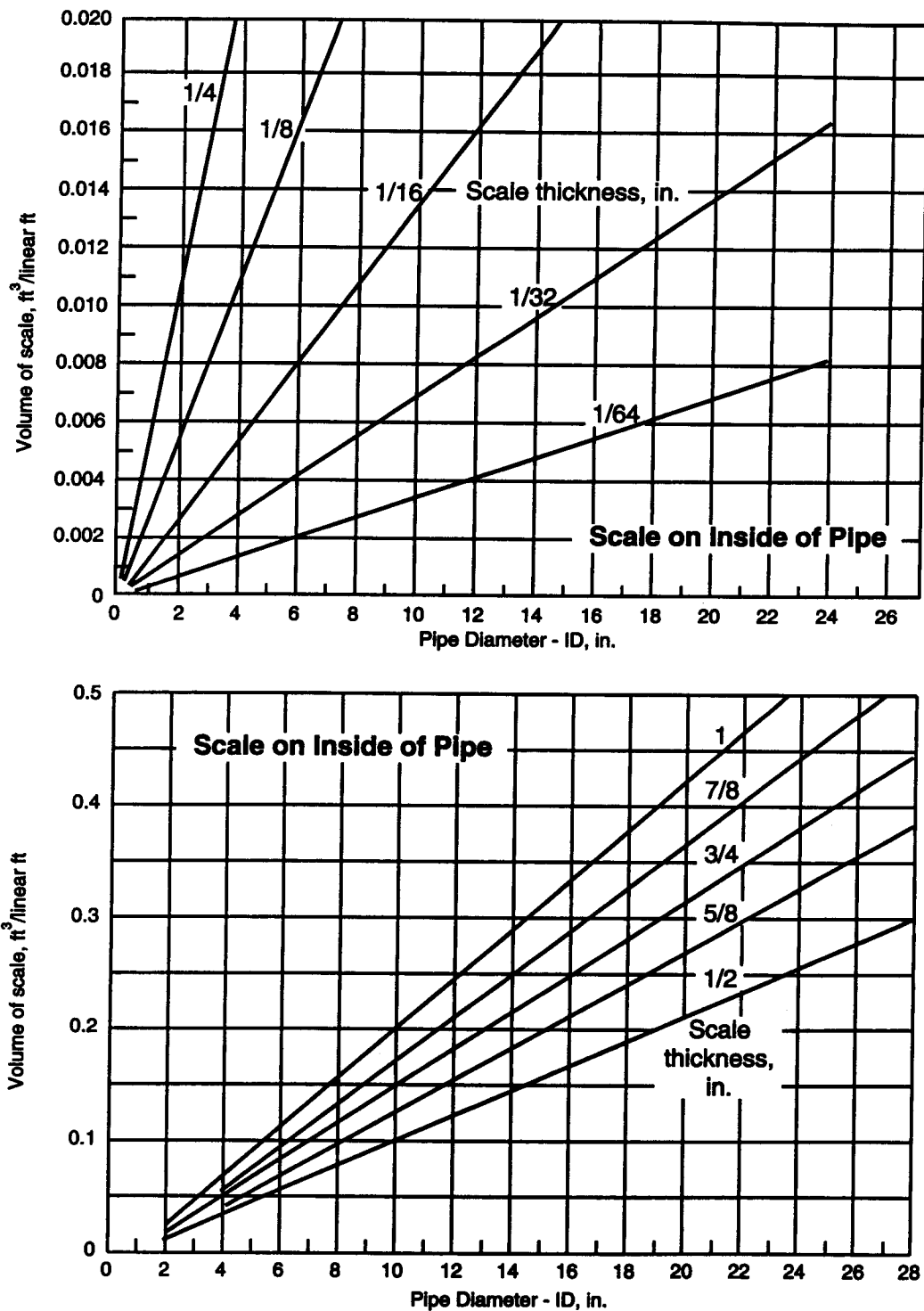


Figure 3.19 Determination of Scale Volume Inside Pipe^(3.41)

Chelation can also occur at the solid surface of the calcium carbonate scale, taking calcium ions directly from the crystal lattice.

The basic disadvantages to the use of chelants to dissolve calcium carbonate scale are:

- Chelating agents are not efficient "solvents." For example, it takes 7.4 ppm EDTA to chelate 1.0 ppm Ca^{++} .
- The chemicals are relatively expensive.

Chelating agents are seldom used to remove calcium carbonate scale in normal oilfield operations. However, their use has been reported in Prudhoe Bay.^(3.42)

Calcium Sulfate (Gypsum)

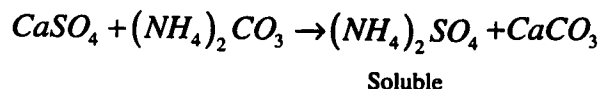
Hydrochloric acid is not a good solvent for CaSO_4 . The maximum solubility of CaSO_4 in HCl is only 1.8 wt % at 25°C and atmospheric pressure.^(3.43)

Converters

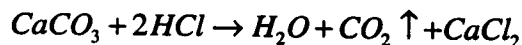
Inorganic Converters

Inorganic converters are usually carbonates or hydroxides which react with calcium sulfate and "convert" it to acid soluble calcium carbonate or calcium hydroxide. The conversion treatment is then followed by a hydrochloric acid treatment to dissolve the resulting calcium carbonate or calcium hydroxide.^(3.44)

A good example of this type of chemical is ammonium carbonate which has been marketed under several trade names. The reaction is:



The calcium carbonate is then dissolved with HCl:



The CO_2 liberated by the acid reaction helps to mechanically dislodge any remaining deposit. Inorganic converters are not recommended for dense deposits and are seldom used.

Organic Converters

Organic converters such as sodium citrate, potassium glycollate, and potassium acetate are also used.^(3.44) These materials react with calcium sulfate deposits causing them to swell and become soft so they may be removed easily by flushing with water. These chemicals are expensive, require several hours contact time to work on thick deposits, and should be checked on an actual sample of the scale before application, if possible.

Chelating Agents

The same comments apply here as for use to remove calcium carbonate.

Sodium Hydroxide (Caustic)

A 10% solution of NaOH will dissolve up to 12.5% of its weight of gypsum scale. *Be careful — caustic burns skin!*

Salt Water

Water containing 55 000 mg/L of NaCl will dissolve three times as much gypsum at 104°F [40°C] as will fresh water at the same temperature.

Barium Sulfate

Dense barium sulfate is almost impossible to chemically remove. However, several proprietary “scale dissolvers” are available which have been used to dissolve thin layers of barium sulfate scale.

These materials are chelating agents rather than true solvents. Barium sulfate has a “solubility” of approximately 0.5 lb per gallon of chemical [120 g/L] in most of the commonly used scale dissolvers. This is rather low for a “solvent” by most standards. In addition, their reaction rates are often slow and their cost is relatively high.

However, they are the only chemicals which have been used successfully for the removal of downhole barium sulfate. Their disadvantages limit their application to the removal of thin layers of scale in systems where extremely large amounts of revenue are at risk, such as the North Sea.

Iron Compounds

Hydrochloric acid is normally used to dissolve iron compounds. Once again, it must contain a corrosion inhibitor to prevent pipe corrosion. In addition, it should contain an iron-stabilizing agent to prevent precipitation of iron compounds once the acid spends.

Iron dissolved during acidizing can exist as either ferric (Fe^{+++}) or ferrous (Fe^{++}) ions. As the acid spends, the pH will rise, and ferric ions will begin to precipitate as $\text{Fe}(\text{OH})_3$ (ferric hydroxide) at a pH of about 2.2.^(3.45) Once the pH reaches a pH of 3.2, essentially all of the ferric iron will have precipitated. Iron stabilizing agents are employed to prevent precipitation of ferric hydroxide.

There are two primary types of iron stabilizers:

- Chelating or Sequestering Agents

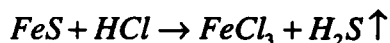
These materials react with ferric ions to form a water soluble complex, thus preventing precipitation. Commonly used chelants are citric acid, acetic acid, mixtures of citric and acetic acids, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid (NTA).

- Reducing Agents

Reducing agents convert ferric ions to the more soluble ferrous ions. Erythorbic acid has been used for this purpose, and is capable of solubilizing up to nine times as much ferric iron as citric acid.^(3.46)

In contrast, ferrous ions are quite soluble at pH values up to 7 and above. Since spent acid usually reaches a maximum pH of about 5.3, precipitation of ferrous iron is seldom a problem.

If iron sulfide is to be dissolved, care is suggested. The reaction between FeS and HCl is:



H_2S is *extremely poisonous* and a few ppm in the air can *kill* you. A toxicity guide is given in Appendix 18. Fresh air masks should be on location and in use if there is any possibility that personnel may breathe any H_2S .

Salt (NaCl)

A fresh water wash is the best medicine for salt deposits.

Sand, Silt, Clay

These are usually present as occluded particles in scale deposits. Once the bulk scale material is dissolved, these materials may be washed out.

Scale Removal from Surface Lines

The Use of Line Scrapers

Scale removal from surface lines is usually accomplished by the combined use of chemicals and line scrapers, or "pigs." The basic types of pigs available are shown in Figure 3.20.^(3,47)

Foam Pigs

Foam pigs are normally used for cleanout of lines which are not routinely pigged. They are made of an open-cell foam with a hard rubber or plastic wrapper. They are also made in brush form.

These pigs can be pumped through a series of lines of different diameters, and the body will deform sufficiently (within limits) to permit the pig to continue to do an effective scraping job.

Foam pigs are available in various lengths and styles. However, the length is usually twice the diameter. Foam pigs form a seal against the inside of the pipe by compressing the foam and do not seal from pressure differential as do the other types of pigs.

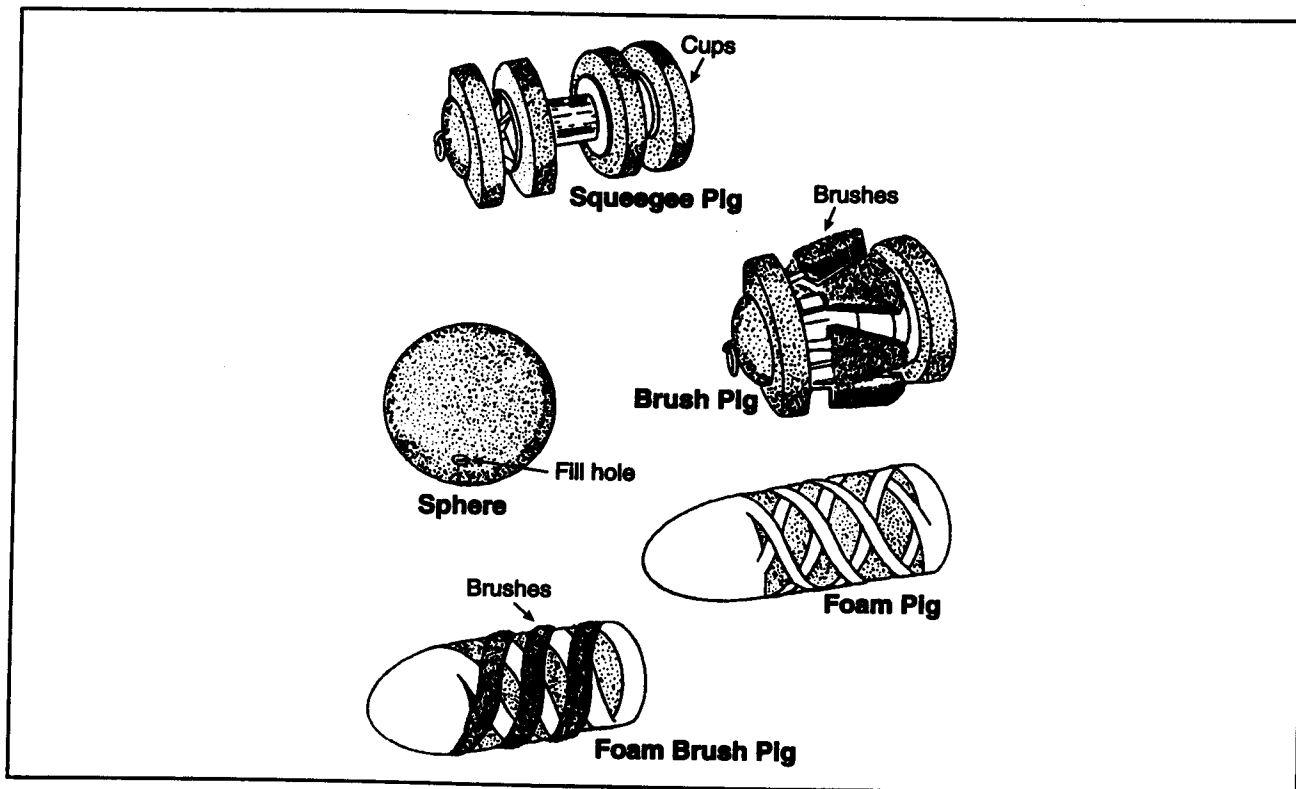


Figure 3.20 Types of Pigs

Brush or scraper pigs have holes in the pig to allow for bypass. Fluid passing through the holes in the pig will disperse the scraped solids in front of the pig. This will prevent a build-up of material in front of the pig which could create a plug and cause the pig to become stuck in the line.

Foam pigs with brushes have a built-in bypass. The brushes are short and fixed to the pig body. The blow-by occurs through the brush and helps to keep the brushes clean. If additional bypass area is necessary, the rubber or plastic covering on the nose of the pig can be cut out allowing passage of liquid through the open-cell foam body. (Figure 3.21)^(3.47)

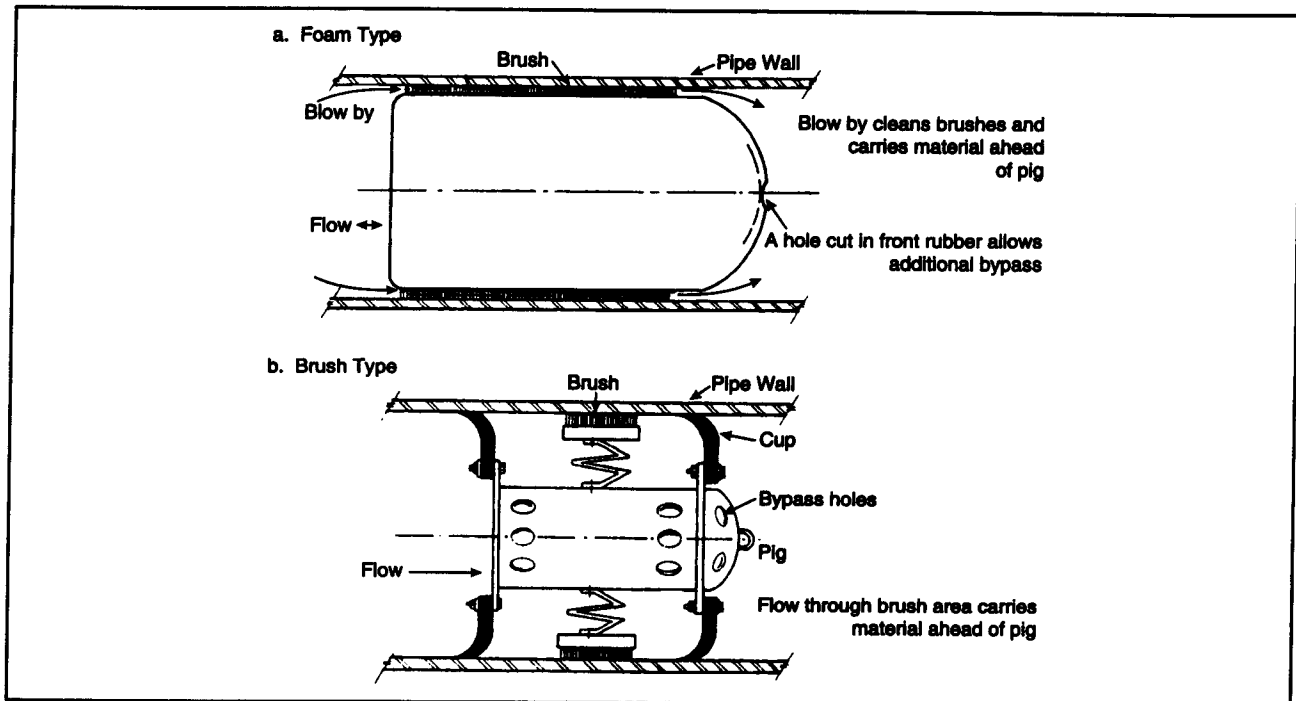


Figure 3.21 Cleaning Pigs

A typical flowline cleanout to remove oil coated calcium carbonate from a line might consist of the following steps:

1. Slug of solvent followed by a pig.
2. Slug of inhibited HCl followed by a pig.
3. Either a neutralizing solution (high pH water) or a thorough water wash to remove all acid. Acid inhibitors break down with time and all acid, spent or otherwise, must be flushed from the line or severe pitting corrosion may result.

Gelled Plugs

Gelled fluids can be injected into a line ahead of a conventional line scraper to aid in the transport of large volumes of solids. For example, a gelled-water and scraper system was used to remove approximately 350 tons of mill scale and other debris from a 280 mile-long, 36-in. OD gas line in the North Sea.^(3.48)

Batches of gelled fluids (Kelzan XC polymer in water) and pipeline scrapers were used to remove loose and loosely adherent rust, silt, welding rods, weld slag, and other debris from the pipeline.

A wide variety of water-base gels, including hydrochloric acid, as well as hydrocarbon-base gels can be formulated to satisfy the specific requirements of a cleaning operation.

When a gelled fluid is in laminar flow in a pipeline, the central portion of the fluid flows as a plug with little exchange between the plug and the annular fluid. The velocity of the central plug can be significantly higher than the mean flow velocity.

A scraper behind a gel forces the fluid in the vicinity of the pipe wall, which contains entrained solids, to move into the central plug-flow region where it is carried forward through the length of the gel batch.

The debris that would remain in front of a mechanical pig in a conventional operation is picked up, carried forward, and eventually circulated and evenly distributed over a relatively long distance. This greatly reduces or eliminates the possibility of sticking the mechanical pig by debris build-up in front.

Downhole Cleanout

Downhole cleanout usually consists of removing scale from the tubing, the perforations, or formation face (open-hole completions) and sometimes from the pore spaces or fractures in the formation matrix.

Removing scale from tubing is basically the same as removal from surface lines, although pigs cannot be used. Except for special boring tools which normally are not used, tubing cleanout must be accomplished by chemical means alone. Obviously, if the tubing is badly scaled or plugged it may be necessary to pull the tubing and clean it on the surface.

Removal of scale from the formation face or perforations usually involves a simple soaking operation with one or more solvents. However, if scale has formed in the perforation tunnels and pore spaces back into the formation for several inches, chemical soaking may not be successful. Here special downhole tools such as casing brushes, surge/swab tools, suction washers, circulation washers or retrievable bridge plugs and squeeze packers may be required in conjunction with a solvent to achieve removal of the scale.

In extreme cases, hydraulic fracturing may be the only way to penetrate the scaled interval.

Downhole scale problems are more prevalent in producing wells than in injection wells. Hence, most of the complex scale cleanout procedures are aimed at producers. It is possible to prevent scaling problems in injection wells. Downhole cleanout should not be a frequent problem in injection systems if they are being monitored properly. It is much easier and cheaper to prevent or treat the problem on the surface than to try to remove downhole deposits after they have formed.

If injection pressures begin to rise and injection well plugging or scaling is indicated, the following is suggested:

1. Try to backflow the well. If suspended particles have simply filtered out the formation face, this alone may solve the problem. If you can backflow the well, be sure and try to catch samples of any solids which come to the surface. If gas is available, a gas-lift valve can be installed in the injection tubing to assist in the periodic backflow of an injection or disposal well.
2. If backflowing is not successful, go to a chemical cleanout procedure.

Technically, it is advisable to swab the solvents back to the surface or backflow the well after treatment. Solvents may become supersaturated and re-precipitate the material just dissolved. If re-precipitation occurs in the wellbore area, serious plugging can result. Thus, cleaning solutions should be brought back to the surface rather than displaced into the formation whenever possible.

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NOTES:

4

CORROSION CONTROL

THEORY OF CORROSION

Most metals are found in nature as metallic oxides or salts. Refining to produce pure metal requires a large energy input. This energy is “stored” and is available to supply the necessary driving force to return the metal to its original state — an oxide or salt. This means that metals are unstable with respect to most environments and have a natural tendency to return to their original lower-energy state, or “corrode.”

Corrosion is an electrochemical process. This means that electrical current flows during the corrosion process. In order for current to flow, there must be a driving force, or a voltage source, and a complete electrical circuit.

Voltage Source

The source of voltage in the corrosion process is the energy stored in the metal by the refining process. Different metals require different amounts of energy for refining and therefore have different tendencies to corrode. This is illustrated in Table 4.1.

TABLE 4.1
Electromotive Force Series for Metals

Energy to Refine	Metal	Potential (Volts)*	Tendency to Corrode
Most Energy	Magnesium	-2.37	Most Eager
	Aluminum	-1.66	
	Zinc	-0.76	
	Iron	-0.44	
	Lead	-0.13	
	Copper	+0.34 to +0.52	
	Silver	+0.80	
Least Energy	Gold	+1.58 to +1.68	Least Eager
* Half-cell potential in solution of own salts, measured with respect to hydrogen reference electrode. ^(4.1)			

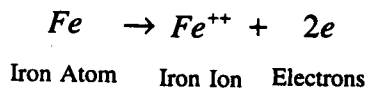
The magnitude of the driving voltage generated by a metal when it is placed in an aqueous solution is called the **potential** of the metal. It is related to the energy that is released when the metal corrodes. Potential values are a function of both the metal and the chemical and physical characteristics of the water. The absolute value of the potential of a given metal is influenced by the water composition, temperature, velocity and many other factors. However, their relative values remain about the same in most solutions of interest. Therefore, magnesium usually has a greater tendency to corrode than does iron in the environments of interest.

The Electrical Circuit

In addition to a source of voltage, there must be a complete electrical circuit. The electrical circuit of the corrosion process consists of four parts.

Anode

The anode is that portion of the metal surface that is corroded. It is the point at which metal dissolves, or goes into solution. When metal dissolves, the metal atom loses electrons and goes into solution as an ion. Since atoms contain equal numbers of **protons** (positively charged particles) and **electrons** (negatively charged particles), the loss of electrons leaves an excess of positive charges, and the resulting ion is positively charged. The chemical reaction for iron is:

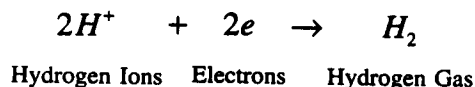


This loss of electrons is called **oxidation**. The iron ion goes into solution and the two electrons are left behind in the metal.

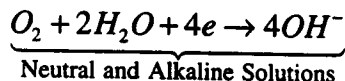
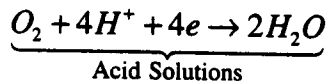
Cathode

The cathode is that portion of the metal surface which does not dissolve, but which is the site of another chemical reaction(s) necessary to the corrosion process. The electrons left behind by the solution of iron at the anode travel through the metal to the cathodic surface area where they are consumed by reaction with ions present in the water. The consumption of electrons is called a **reduction reaction**.

Typical reactions are:



Or if oxygen is present two other reactions are also possible:



Thus, the reaction at the anode areas produces electrons and the reaction(s) at the cathode areas consumes the electrons. This is the essential feature of an electrochemical reaction: electrons are generated by a chemical reaction at one point, and then travel to another point where they are consumed by another reaction. As you may recall, electrical current flow is actually the passage of electrons from

one point to another. Convention says that the electrical current flows in the opposite direction of electron travel. Thus, as electrons flow from the anode area to the cathode area, electrical current flows through the metal in the opposite direction, from the cathode to the anode.

Electrolyte

In order to support the reactions previously listed and to complete the electrical circuit, the metal surface (both the anode and the cathode) must be covered with an electrically conductive solution. Such a solution is called an *electrolyte*. Water is an electrolyte which increases in electrical conductivity as the amount of dissolved salts or ions increases. The electrolyte conducts current from the anode to the cathode.

Electron Conductor

The anode and the cathode must be connected by something which will conduct electrons (electrical current) in order to complete the circuit and provide a path for current to flow from the cathode back to the anode. In the case of a corroding metal surface, the metal itself is the electron conductor.

This combination of anode, cathode, electrolyte, and electron conductor is called a *corrosion cell*. A schematic of the corrosion process for iron is shown in Figure 4.1. This sketch is merely an illustration. Metal atoms do not necessarily dissolve at a single point on a metal surface, nor are cathode areas restricted to one area on the surface. In the case of localized corrosion, such as pitting, these processes are limited to localized areas. However, in the case of general corrosion the reactions occur randomly over the metal surface.

At this point in the study of corrosion a key question arises, "Why do certain areas of the metal surface act as anodes?" The answer is not a simple one. However, in most cases the reason centers on inhomogeneities in the metal surface, in the electrolyte, or both.

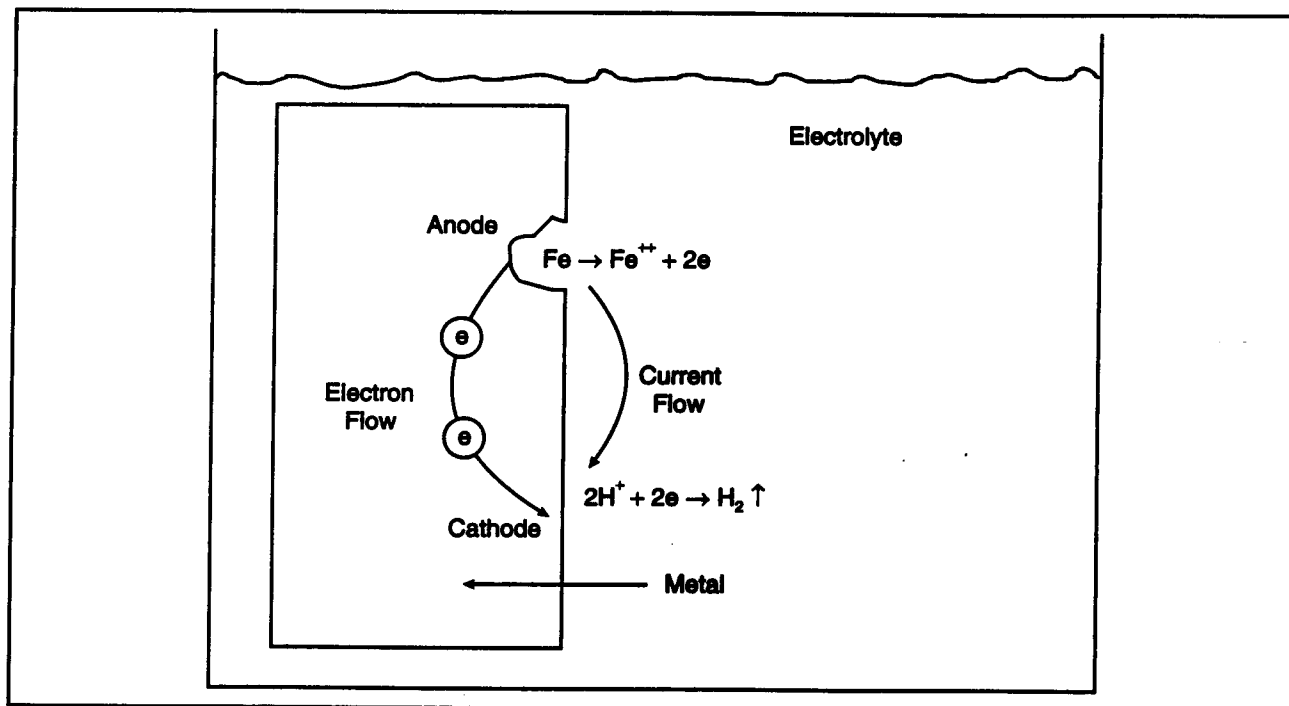


Figure 4.1 The Corrosion Cell

THE NATURE OF METALS

Commercial metals are not homogeneous, but contain inclusions, precipitates, and perhaps several different phases. When the metal is placed in an electrolyte, potential differences exist between these phases, resulting in corrosion cells on the metal surface.

For example, steel is primarily an alloy of iron and carbon. Pure iron is a relatively weak, ductile material. When it is alloyed with small amounts of carbon (usually 0.2 to 1.0 per cent), a much stronger material is created. However, as a result of reacting part of the iron with carbon, we now have a metal composed of two materials: pure iron and iron carbide (Fe_3C), the product of the iron-carbon reaction. The iron carbide is distributed within the iron as tiny microscopic islands, and these islands of iron carbide have a lower tendency to corrode than does the pure iron. The Fe_3C and the pure iron are in intimate contact (allowing electron flow), so when the steel is placed in water (an electrolyte), the electrical circuit is complete and current flows through thousands of tiny microcells on the steel surface. The pure iron acts as the anode and corrodes, while the Fe_3C acts as the cathode.

If we were to look through a microscope and concentrate on two adjacent grains of Fe and Fe_3C on the surface of a piece of steel immersed in water, it might look like Figure 4.2.

This condition may change with time. As corrosion products accumulate, the potential distribution on the metal surface may change, shifting the anodic areas.

Intergranular attack is caused or accelerated by potential differences between the grains and grain

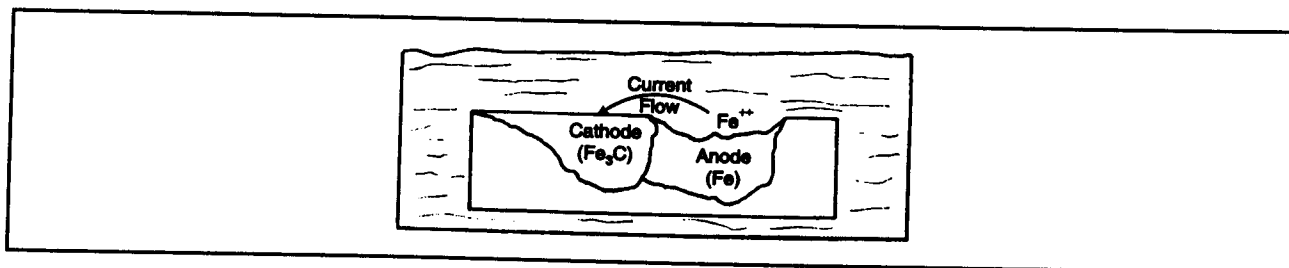


Figure 4.2 Fe- Fe_3C Corrosion Cell

boundaries. Local heating can result in changes of the nature of phases or their compositions creating differences in potential, such as in weldline corrosion.^(4.2)

Thus, metals are inherently inhomogeneous materials, and potential differences on the metal surface are a natural result. These differences are one of the primary causes of corrosion.

The important thing to realize is that current flows during the corrosion process, and the amount of current flowing is a measure of the severity of the corrosion. It is dependent on both the nature of the metal and the type of environment, or electrolyte. One ampere of corrosion current flowing for one year represents the loss of twenty pounds of iron.

THE EFFECT OF METAL COMPOSITION

As previously stated, different metals have different tendencies to corrode. However, a discussion of a wide range of metals is not really warranted here. Steel is the primary metal used in the oilfield and so we will stick pretty closely to the subject of how and why water corrodes steel.

There are, of course, many "steels." Simple low carbon steel is universally used in production operations for lines, tubing, tanks and treaters. However, some steels containing chromium and nickel (which add corrosion resistance), and some non-ferrous alloys (contain no iron) are used in a few items such as pumps and valves.

NACE Standard RP0475, "*Selection of Metallic Materials to be Used in All Phases of Water Handling for Injection into Oil Bearing Formations*," is an extremely useful guide to materials selection for water injection systems.^(4.3)

EFFECT OF WATER COMPOSITION

Conductivity of Water

As previously stated, the corrosivity of water increases as the conductivity increases. Distilled water is not very conductive and is not very corrosive. Salt water is quite conductive and is corrosive. The corrosivity increases as the water gets saltier.

pH of Water

The corrosivity of the water usually increases as the pH decreases (becomes more acidic). At higher pH values protective scales (iron hydroxide, or carbonate scale) may form on the steel surface and prevent or slow down further corrosion.

Dissolved Gases

Oxygen, carbon dioxide or hydrogen sulfide dissolved in water drastically increases its corrosivity. In fact, dissolved gases are one of the primary causes of most corrosion problems. If they could be excluded and the water maintained at a neutral pH or higher, most water systems would have very few corrosion problems.

Dissolved Oxygen

Of the three dissolved gases mentioned, oxygen is by far the worst of the group. Figure 4.3 illustrates the effect of oxygen concentration and temperature on the corrosion rate of low carbon steel in tap water.^(4.4)

It is possible to estimate the corrosion rate of mild steel in fresh water using an equation developed by Pisigan and Singley.^(4.5) The equation is empirical, and is based on a correlation between the corrosion rate of mild steel and several analytical parameters.

$$mpy = \frac{TDS^{0.253} DO^{0.820}}{(10^{SI})^{0.876} Day^{0.373}} \quad (4.1)$$

Where: TDS = Total dissolved solids, mg/L
 DO = Dissolved oxygen concentration, mg/L
 SI = Langelier Saturation Index (See Chapter 3)
 Day = Coupon exposure period, days

This equation applies only to the experimental conditions employed in this study, which are summarized in Table 4.2. The corrosion rates were calculated from the weight loss of mild steel coupons in

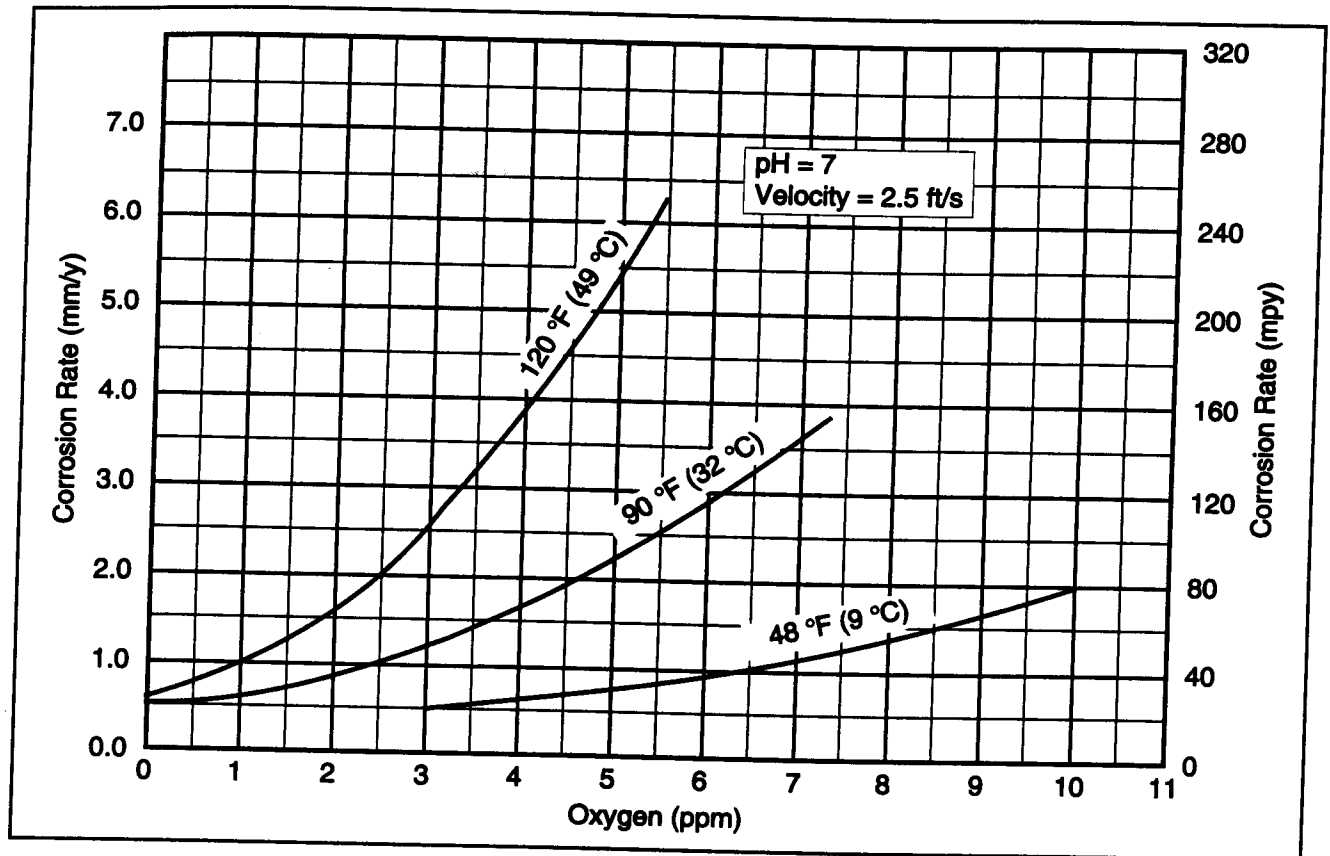


Figure 4.3 Corrosion of Steel in Tap Water

TABLE 4.2
Means and Ranges of Data

Parameter	Mean	Range
TDS, mg/L	473	116-791
Ca ⁺⁺ , mg/L	68	10-120
Mg ⁺⁺ , mg/L	16	2-52
Na ⁺ , mg/L	64	7-130
Cl ⁻ , mg/L	119	18-213
SO ₄ ⁼ , mg/L	79	16-208
Alkalinity, mg/L as CaCO ₃	116	21-232
pH, units	7.77	6.70-8.95
pHs, units	7.79	7.60-9.07
Langelier Index, units	-0.02	-2.12-1.90
Ionic Strength, moles/L	0.0081	0.0001-0.0198
Dissolved Oxygen, ppm	5.1	1.4-9.1
Corrosion Rate, mpy	11.9	2.1-36.6
Corrosion Rate, mm/yr	0.301	0.053-0.930

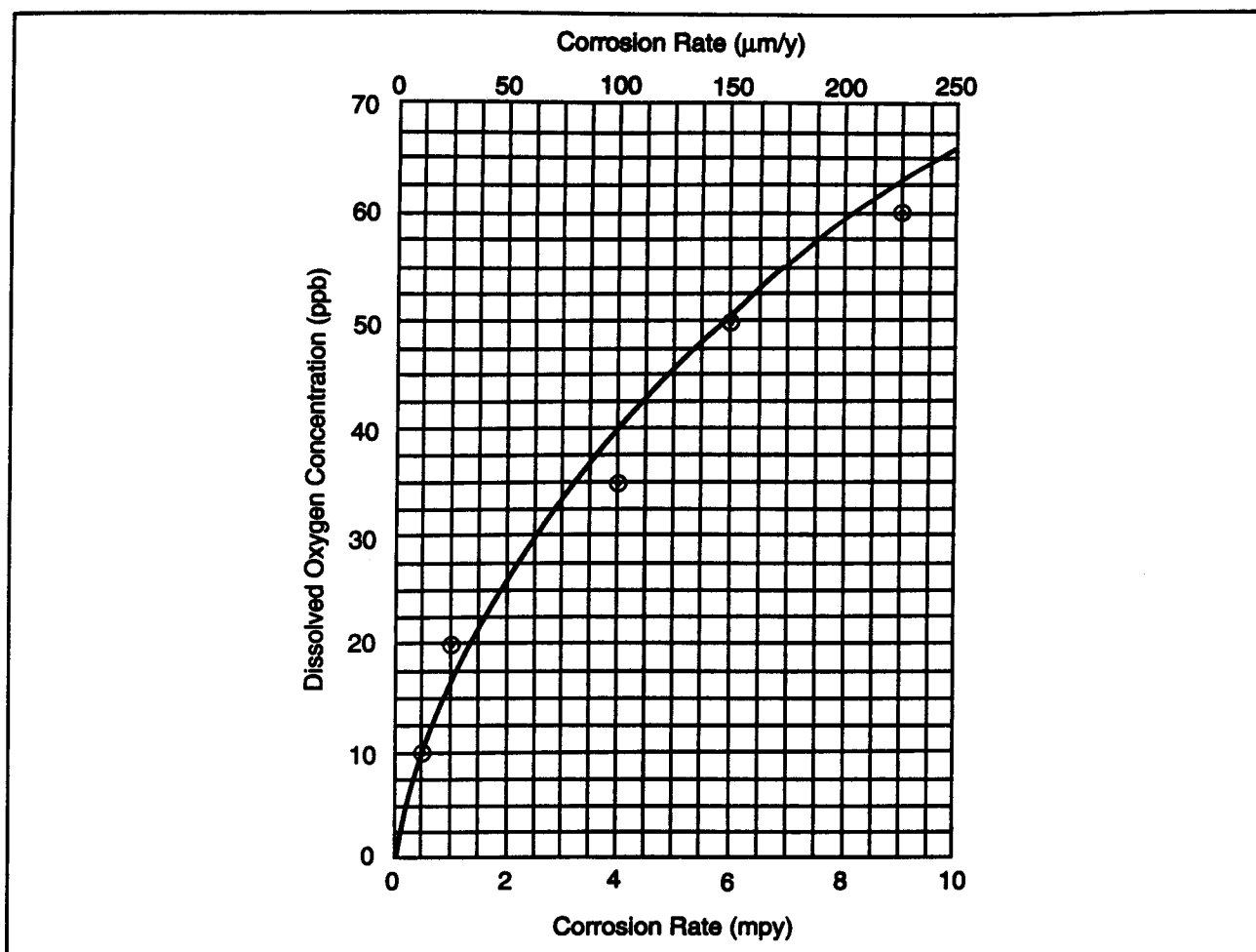


Figure 4.4 Effect of Oxygen Concentration on Corrosion Rate

jars which were stirred at 30 rpm. A total of seventeen waters were used in the study, which was conducted at a temperature of $20 \pm 3^\circ\text{C}$. This equation does not consider temperature or velocity as variables.

Dissolved oxygen can cause severe corrosion at extremely low concentrations. Figure 4.4 shows measured corrosion rates of mild steel as a function of dissolved oxygen concentration in sulfide-free produced water being injected at Huntington Beach, California.^(4.6)

If dissolved H_2S and/or CO_2 are present, even trace quantities of dissolved oxygen will drastically increase their corrosivity.

Oxygen is not present in produced water, but often comes in contact with it after it is brought to the surface. Water from lakes or streams will be saturated with oxygen, and water from shallow wells may contain some oxygen. Whenever possible, it should be rigorously excluded.

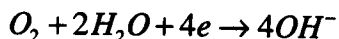
The solubility of oxygen in water is a function of pressure, temperature, and the chloride content. Oxygen is less soluble in salt water than in fresh water. (See Figure 6.1)

Oxygen corrosion occurs as follows:

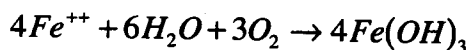
Anode Reaction



Cathode Reaction (in neutral or alkaline waters)



or, combining the two



If the pH is above 4, ferric hydroxide is insoluble and precipitates.

Oxygen accelerates corrosion drastically under most circumstances. It does so primarily by acting as a "cathodic depolarizer." This means that it will easily combine with electrons at the cathode and allow the corrosion reaction to proceed at a rate limited primarily by the rate oxygen can diffuse to the cathode. Without oxygen, the corrosion reaction is limited by the rate it can dispose of electrons by reaction with other species in the water such as hydrogen ions. When oxygen is present, it is an additional and eager consumer of electrons at the cathode surface, which results in accelerated corrosion.

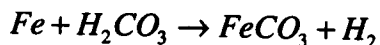
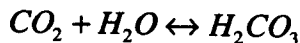
Oxygen attack is usually pitting in nature.

It is important to realize that the corrosivity of "pure" water increases as the dissolved oxygen content increases — up to a point. If there is sufficient oxygen in the water, the $Fe^{++} \rightarrow Fe^{+++}$ oxidation may occur very rapidly, before the Fe^{++} ions have a chance to diffuse away from the metal surface. In this case $Fe(OH)_3$ can form on the metal surface and become protective.^(4.4) However, in most oilfield waters sufficient chloride ions are present to interfere with the formation of a protective film and corrosion rates continue to increase with oxygen concentration.

Concentration cells, or differential aeration cells, can cause preferential attack or pitting. Any time there is a difference in the oxygen content of water in two adjacent areas in a system, attack will take place preferentially in the area exposed to the *lowest* oxygen concentration. Typical examples are water-air interfaces, crevices and "oxygen tubercles" in water systems.

Dissolved Carbon Dioxide

When carbon dioxide dissolves in water it forms carbonic acid, decreases the pH of the water and increases its corrosivity. It is not as corrosive as oxygen, but usually results in pitting. Corrosion caused by carbon dioxide dissolved in water is called "sweet" corrosion.



The solubility of CO_2 in water, like all gases, is a function of the partial pressure of CO_2 in the atmosphere above the water. The greater the partial pressure, the greater the solubility. Therefore, in two-phase systems (gas + water), corrosion rates go up as the partial pressure of CO_2 increases. The effect of CO_2 partial pressure on the corrosion rate of mild steel in distilled water is illustrated in Figure 4.5.^(4.7)

DeWaard and Milliams^(4.8) measured the corrosion rate of X-52 carbon steel in an oxygen-free solution of 0.1% (1000 ppm) NaCl saturated with CO_2 at partial pressures from 0.7 to 15 psi [5-103

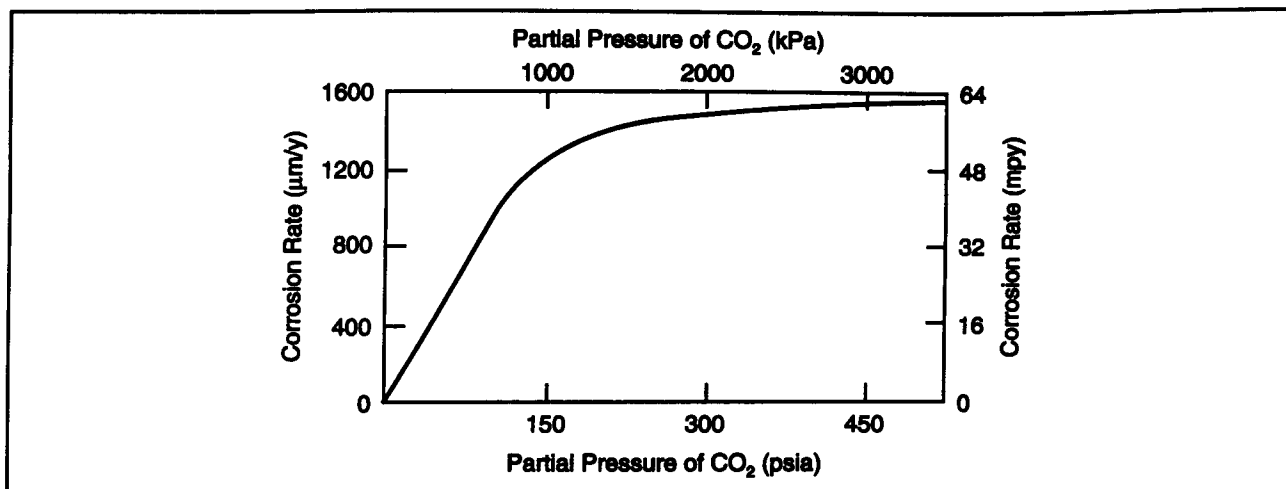


Figure 4.5 Effect of CO₂ Partial Pressure on Corrosion Rate^(4.7)

kPa] over a temperature range of 41-176°F [5-80°C]. Both polished and grit-blasted steel specimens were used. The solution was stirred to achieve a velocity of about 3 ft/second [0.9 m/s].

Based on the measured corrosion rates, they developed an equation to predict “worst case” *uniform* corrosion rates. The equation was subsequently modified to read as follows:^(4.9)

$$\log CR = 5.8 - \frac{1710}{T} + 0.67 \log(pCO_2) \quad (4.2)$$

Where:

CR = Corrosion rate, mm/y

T = Temperature, °K (°K = °C + 273)

pCO₂ = Partial pressure of CO₂, bar

This equation is presented in the form of a nomograph in Figure 4.6. A scale factor of 1 is suggested for brines.

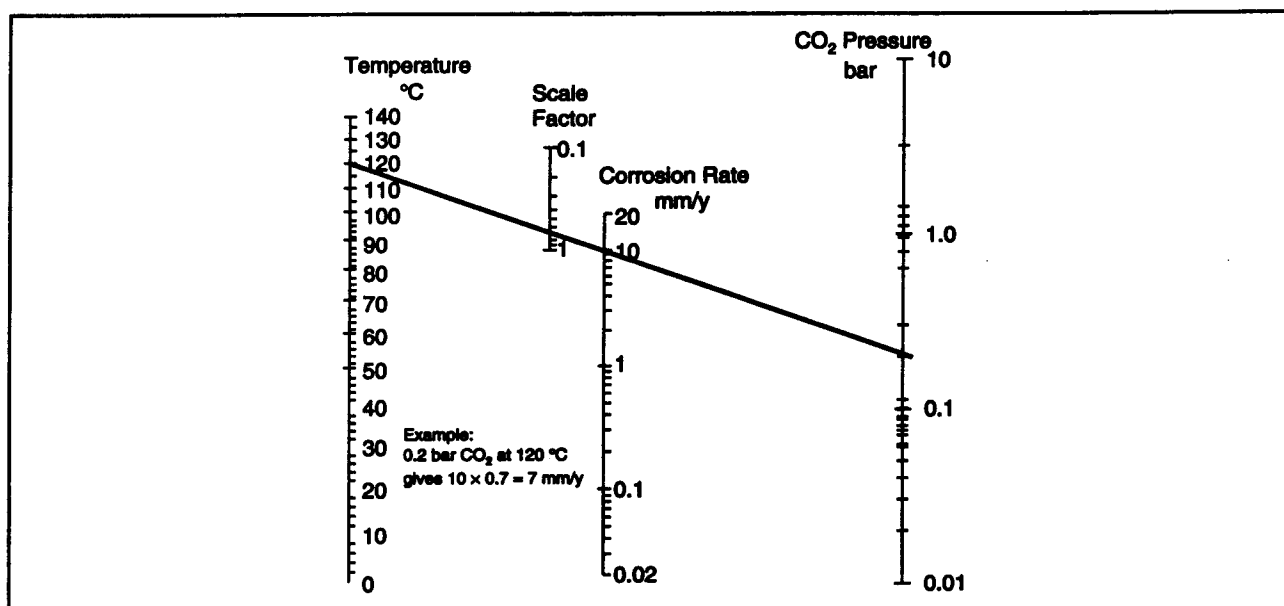


Figure 4.6 CO₂ Corrosion Rate Prediction^(4.9)

The corrosion rates measured at high CO₂ partial pressures are extremely high. It is likely that in most cases these high rates will not persist very long in operating systems due to the formation of a layer of corrosion product on the metal surface. As a corrosion product layer forms, uniform corrosion decreases, but pitting can become an extremely severe problem.

Equation 4.2 can be used for low TDS waters in air-free, sweet, two-phase (gas + water) systems to estimate the maximum uniform corrosion rates of a bare-steel surface in the absence of an iron carbonate corrosion product film.

As temperatures increase, a protective layer of iron carbonate *may* form on the surface and slow down the rate of corrosion. It is extremely difficult to predict whether or not a *protective* iron carbonate scale will form, and if so at what temperature, because it is a function of many factors including CO₂ partial pressure, velocity, and water composition. In many cases, the iron carbonate scale is not protective, and accelerated corrosion is observed beneath the scale.^(4.9-4.11)

In addition, the presence of liquid hydrocarbons *may* reduce corrosion under certain conditions.^(4.12)

In water systems containing bicarbonate alkalinity, the amount of CO₂ present to cause corrosion is a function of pH due to the CO₂-bicarbonate-carbonate equilibria discussed in Chapter 3.

As previously mentioned, the presence of any oxygen increases the corrosivity of CO₂.

Dissolved Hydrogen Sulfide

Hydrogen sulfide is very soluble in water, and when dissolved behaves as a weak acid.



The degree of dissociation is a function of pH and is illustrated in Figure 4.7. At normally encountered pH values, sour waters will contain a mixture of H₂S and HS⁻. (HS⁻ is the bisulfide or hydrosulfide ion.)

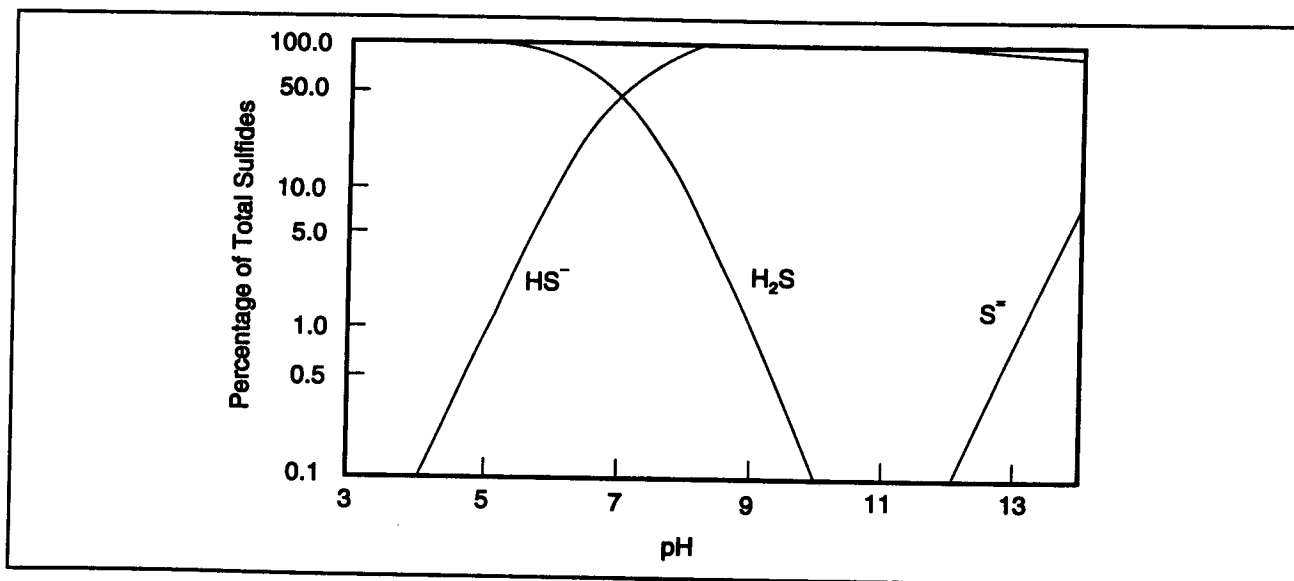
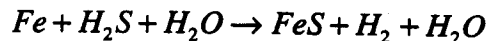


Figure 4.7 Ionization of H₂S in Water as a Function of pH

Corrosion caused by H_2S dissolved in water is called "sour" corrosion and is usually pitting in nature. The general corrosion reaction is:



The iron sulfide corrosion product is extremely insoluble and usually adheres to the steel surface as a scale. It is an excellent electron conductor and is cathodic to the underlying steel. The steel and iron sulfide thus form a galvanic couple which tends to accelerate the corrosion at defects in the scale. Deep pitting is the normal result.

The combination of H_2S and CO_2 is more aggressive than H_2S alone and is frequently found in oilfield environments. Once again, the presence of even minute quantities of oxygen can be disastrous.

Other types of corrosion damage can also occur in sour systems: sulfide stress cracking (SSC), hydrogen blistering, and a specialized form of hydrogen blistering called hydrogen induced cracking (HIC). These forms of corrosion are discussed later in this chapter.

Hydrogen sulfide can also be generated in water systems by sulfate reducing bacteria. This will be discussed in greater detail in Chapter 5.

Organic Acids

Produced waters usually contain organic acids, such as acetic acid. In low concentrations acetic acid is extremely corrosive, with an attack approximately as severe as that of hydrochloric or sulfuric acid.

Physical Variables

Water Temperature

Corrosion rates usually increase as temperature increases because all of the reactions involved speed up.

In a system open to the atmosphere, corrosion rates may increase at first and then with a further temperature increase, the corrosion rate may drop off due to dissolved gases coming out of solution. If the system is closed, the corrosion rate will continue to increase with temperature because the dissolved gases have no place to go.

Figure 4.8 illustrates the effect of temperature on the corrosion rate of mild steel in water containing dissolved oxygen.

When the water contains bicarbonates, increases in temperature will promote scale formation which may slow down the corrosion reaction. However, if the temperature is high enough, it can also lead to decomposition of bicarbonates and produce additional CO_2 .

System Pressure

Pressure also has an effect on chemical reactions. In the case of two-phase water systems (water + gas), the primary importance of pressure is its effect on the solubility of dissolved gases. More gas goes into solution as the pressure is increased resulting in increased corrosion rates.

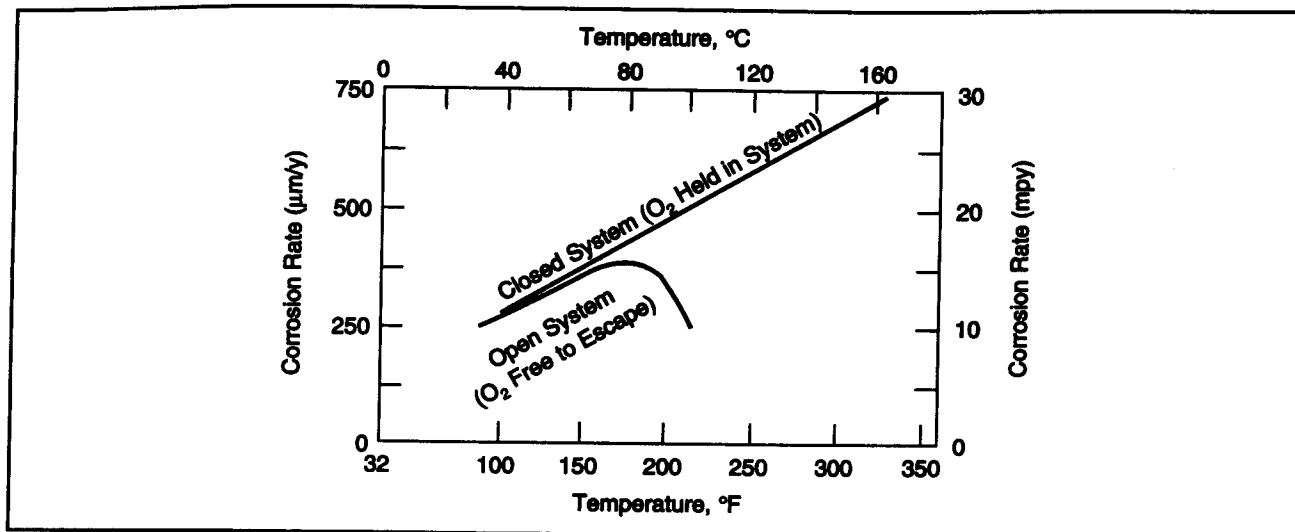


Figure 4.8 Effect of Temperature on Corrosion Rate (4.13)

Water Velocity

Stagnant or low velocity water usually gives a low general corrosion rate, but pitting is more likely. The fluid velocity should be high enough to keep the majority of any solids entrained in the fluid and prevent excessive deposition in the system. The obvious consequences of solids deposition are the creation of sites for concentration cells and bacterial growth beneath the deposits. Even if solids deposition is minimal, bacterial activity is always more likely in low velocity areas such as tanks and filters. (4.14)

Corrosion rates usually increase with velocity. This is due to the fact that increased fluid velocity speeds up the transport of diffusion-limited species to and from the metal surface. (4.15) For example, the movement of dissolved oxygen to the metal surface to participate in the corrosion reaction is controlled by diffusion, and increased velocity accelerates corrosion caused by dissolved oxygen.

Figure 4.9 shows the effect of velocity on the corrosion rate of mild steel in seawater at ambient temperature exposed for 38 days.

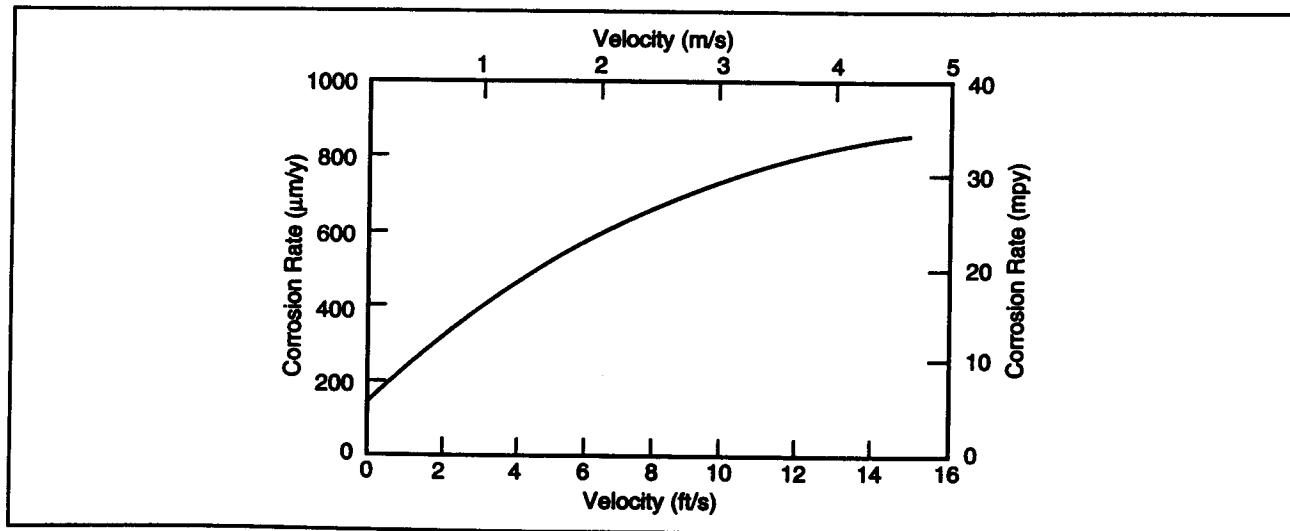


Figure 4.9 Effect of Velocity on Seawater Corrosion (4.16)

If the velocity is too high, erosion, erosion-corrosion, or impingement may result. These problems can be especially severe if the water contains large amounts of suspended solids, and are usually worst at changes in direction, such as elbows. Partially protective corrosion product films are constantly removed or eroded away, leaving a bare metal surface which eagerly corrodes.

Erosional Velocity

The *erosional velocity* above which erosion may occur can be estimated from an empirical equation presented in API RP 14E. *The equation has no demonstrated relationship with corrosion.* However, if the fluid is corrosive, the onset of erosion has a catastrophic effect on the rate at which steel disappears.

$$V_e = \frac{C}{\sqrt{\rho}} \quad (4.3)$$

Where: V_e = Maximum allowable velocity, ft/sec, above which erosion would be expected to occur for a clean, solids-free fluid

C = A constant, typically 100-125

ρ = Density of fluid at flowing pressure and temperature, lb/ft³

This equation was originally developed by the United States Navy during World War II. Based upon tests with solids-free fluids they arrived at a value of $C = 160$. However, the API recommends C values of 125 for intermittent flow and 100 for continuous flow. This equation is used for gas/liquid mixtures as well as liquids.

If the fluid contains significant amounts of suspended solids, many operators use values of C less than 100.

For water, the equation becomes:

$$V_e = \frac{C}{\sqrt{62.4 \times S.G.}} \quad (4.4)$$

Assuming that the water has a specific gravity of 1.0, we can solve the equation for several assumed values of C to examine the range of probable erosional velocities as shown in Table 4.3.

TABLE 4.3
Erosional Velocities

C	V_e	
	ft/s	m/s
160	20.3	6.2
125	15.8	4.8
100	12.7	3.9
80	10.1	3.1

Thus, based on Equation 4.4, it is unlikely that *pure erosion* would constitute a major problem in most water injection systems, regardless of the value of C which is chosen.

High velocities are usually not an issue in systems where the fluid must be pumped considerable distances, as the pump horsepower required to overcome friction losses at higher velocities tends to be excessive. However, high velocities are common in some compact offshore water injection systems where distances are short and the volumes injected are large.

Pipelines

Experience gained in the United States in small diameter piping, typically in the range of 2-8 in. [5-20 cm], indicates that **typical velocities** of 3-5 ft/sec [1-1.5 m/s] are acceptable for water injection systems,^(4.12) and at least one author advocates a range of 2-7 ft/sec (0.6-2.1 m/s).^(4.18)

The advent of very large seawater injection systems in the Middle East and elsewhere has made it very difficult to economically design an injection system within these velocity limits, and velocities in the range of 7-12 ft/sec (2.1-3.6 m/s) are common.^(4.19)

In most systems, the primary problem is that the injection lines are oversized in certain parts of the system, resulting in very low velocities. A minimum velocity of 3 ft/s (1 m/s) is recommended for water injection lines.

Velocities high enough to cause erosion problems occur much less frequently.

Vessels

Velocities are typically low in vessels, making solids accumulation a virtual certainty. This inevitably results in increased corrosion rates and bacterial activity beneath the solids. To make matters worse, chemicals such as corrosion inhibitors and biocides have limited effectiveness because the accumulated solids prevent them from reaching the metal surface.

All vessels should be designed to facilitate solids removal. For example, cone-bottomed tanks equipped with an internal jetting system and center drain permit regular solids removal without a system shut-down or vessel entry.

High-Low Velocity Areas

Systems may contain adjacent areas which are exposed to different water velocities. If no oxygen is present, the high-velocity area is anodic to the low velocity area and corrodes. If oxygen is present, the low-velocity area receives less oxygen, acts as the anode, and corrodes.

Increased velocity in an oxygenated system can cause an initial increase in corrosion rate (supplies more oxygen), then actually slow the reaction as the velocity is further increased due to formation of $\text{Fe}(\text{OH})_3$ on the metal surface. A further increase may rip the protective film off of the surface

FORMS OF CORROSION

Corrosion may be uniform in nature, resulting in uniform thinning, or it may be localized in the form of discreet pits or larger localized areas. Localized corrosion is usually the most disastrous and the toughest to detect.

Localized attack takes several different forms and is caused by a variety of different situations.

Galvanic Corrosion

When two different metals are placed in contact in an electrolyte, the corrosion rate of the more reactive metal will usually increase and the corrosion rate of the less reactive metal will decrease. This form of corrosion is referred to as bimetallic or galvanic corrosion.

In a galvanic couple, the more active metal is referred to as the anode and the less reactive metal is referred to as the cathode. One of the most important factors in galvanic corrosion is the ratio of the

exposed area of the cathode to the exposed area of the anode. This is referred to the "area effect." The most unfavorable ratio is a large cathode connected to a small anode.

If there is a marked tendency of one metal to corrode in preference to another, such as iron and copper exposed in aerated salt water, the less resistant metal suffers the entire corrosion. Thus, steel rivets in Monel or copper sheet corrode very rapidly; Monel rivets in steel plate cause little damage.

Accelerated corrosion due to galvanic effects is usually greatest near the junction of the two metals.

Mill scale is less reactive than steel, so if pipe is covered with mill scale, which is subsequently partially removed or knocked off, the mill scale will act as the cathode and the bare steel will act as the anode and corrode.

A similar phenomenon often occurs when new pipe is connected to old pipe, especially in external corrosion. The new pipe acts as the anode and corrodes preferentially.

This principle is utilized in a beneficial way in cathodic protection. Steel is connected to a more reactive metal, such as magnesium, and is "protected" (does not corrode). The steel has become a cathode and the more reactive metal the anode.

Preferential Weld Corrosion

Galvanic corrosion frequently occurs in or adjacent to welds. Accelerated corrosion has been observed both in the weld metal and in the heat affected zone (HAZ) adjacent to the weld. Minor differences in chemistry between the weld material and the line pipe are considered the primary cause of this problem.^(4,16) Improper post-weld heat treatment can also be responsible for accelerated corrosion in the HAZ.

Concentration Cells

Localized corrosion can also be created by differences in electrolyte composition at two adjacent points on the metal surface.

Crevice Corrosion

Crevices promote the formation of concentration cells. This is especially serious in oxygenated systems where the oxygen in the crevice may be consumed more rapidly than fresh oxygen can diffuse into the crevice. This causes the pH in the crevice to decrease, resulting in a more acidic environment, which accelerates corrosion.

Air-Water Interface

The water at the surface contains more oxygen than the water slightly below the surface. The difference in concentrations will cause preferential attack at the water line.

Oxygen Tubercles

This is a form of pitting which results from the same type of mechanism as crevice corrosion. It is encouraged by the formation of a porous layer of iron oxide or hydroxide which partially shields the steel surface.

Scales and Sludges

The deposition of any solid on a metal surface which is not sufficiently tight and non-porous to completely protect the metal surface can cause increased corrosion under the deposit due to differential concentration. Even tight, adherent scales can create problems if they form only in spots rather than uniformly over the metal surface. Sulfate reducing bacteria thrive under scales and sludges, creating H_2S and causing localized pitting.

Erosion-Corrosion and Impingement

The formation of a layer of corrosion product on the surface of a corroding metal usually results in decreased corrosion rates. The corrosion product acts as a rather poor coating and partially protects the surface.

Removal of the corrosion product by erosion due to high velocities, turbulence, or the abrasive action of suspended solids can result in increased corrosion rates by continually exposing fresh metal to the electrolyte. This form of corrosion is called erosion-corrosion and is a common cause of failure. Carbon steels are particularly susceptible to this form of attack when the corrosion products which form are soft and easily removed, such as iron carbonate.

Erosion-corrosion normally occurs in localized areas such as bends or elbows. However, it can be fairly widespread in a system if significant amounts of suspended solids are present.

Several equations have been proposed for the calculation of the minimum velocity for the onset of erosion-corrosion,^(4,21) but none have been proven to date. At this time we can simply state that corrosion rates are generally much more severe when flow rates are in excess of the erosional velocity.

A phenomenon similar to erosion-corrosion, but even more localized is known as impingement. This occurs when a stream impinges upon a metal's surface and breaks down protective films at very small areas, resulting in pits or holes at the points of impingement.

Cavitation

Cavitation is caused by the repeated formation and subsequent collapse of vapor bubbles in a liquid on a metal surface. Cavitation damage is a frequent problem in centrifugal pump impellers, the fluid ends of plunger pumps and downstream of throttling valves.

In order for cavitation to occur, the pressure must first drop sufficiently to allow the water to vaporize. The pressure must then increase sufficiently to collapse the bubbles of water vapor. Repeating this process at high speed, such as in the case of a pump, vapor bubbles form and collapse rapidly. Calculations have shown that rapidly collapsing vapor bubbles produce shock waves with pressures as high as 60 000 psi (415 000 kPa). Forces this high can cause damage in two ways:

- Any protective corrosion product films are destroyed at the point of bubble collapse resulting in increased corrosion.
- The force is sufficient to physically tear metal particles from the surface.

Thus, in a corrosive fluid cavitation damage is the result of both corrosion and mechanical effects.

Figure 4.10 shows a pressure profile in a centrifugal pump. If the minimum pressure is low enough to permit the formation of vapor bubbles and the impeller creates sufficient pressure to collapse them, cavitation will occur.

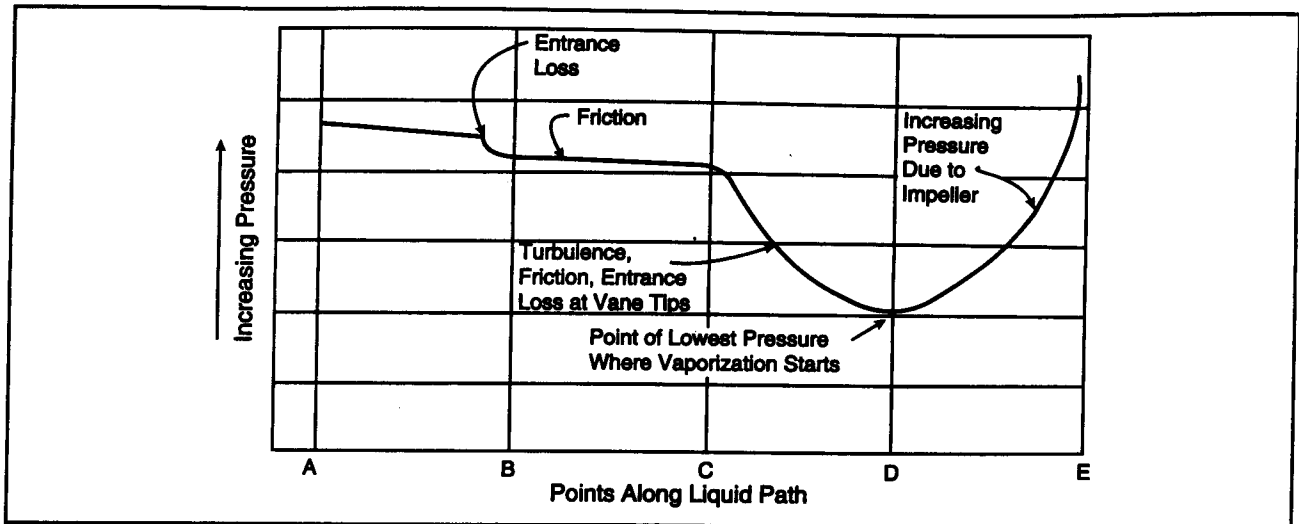


Figure 4.10 Relative Pressures in the Entrance Section of a Centrifugal Pump

Stated differently, the available net positive suction head (NPSH) at the suction flange of the pump must be greater than the NPSH required by the pump to prevent any vaporization of the liquid as it flows from the pump suction flange into the impeller inlet vanes.

The available NPSH can be calculated as outlined by Abbott.^(4.22) Vlaming^(4.23) presents a method for estimating the NPSH required for centrifugal pumps, and Miller^(4.24) discusses NPSH effects on reciprocating pumps.

Cavitation can also occur immediately downstream of control valves. When fluid passes through a restriction, it accelerates and the pressure drops as shown in Figure 4.11.^(4.25) It is possible for the pressure at the vena contracta (point of minimum fluid stream cross section) to drop below the vapor pressure of the liquid, allowing vapor bubbles to form. Once past the vena contracta the liquid decelerates, and if the downstream pressure increases to exceed the vapor pressure, the bubbles will collapse, and cavitation will occur.

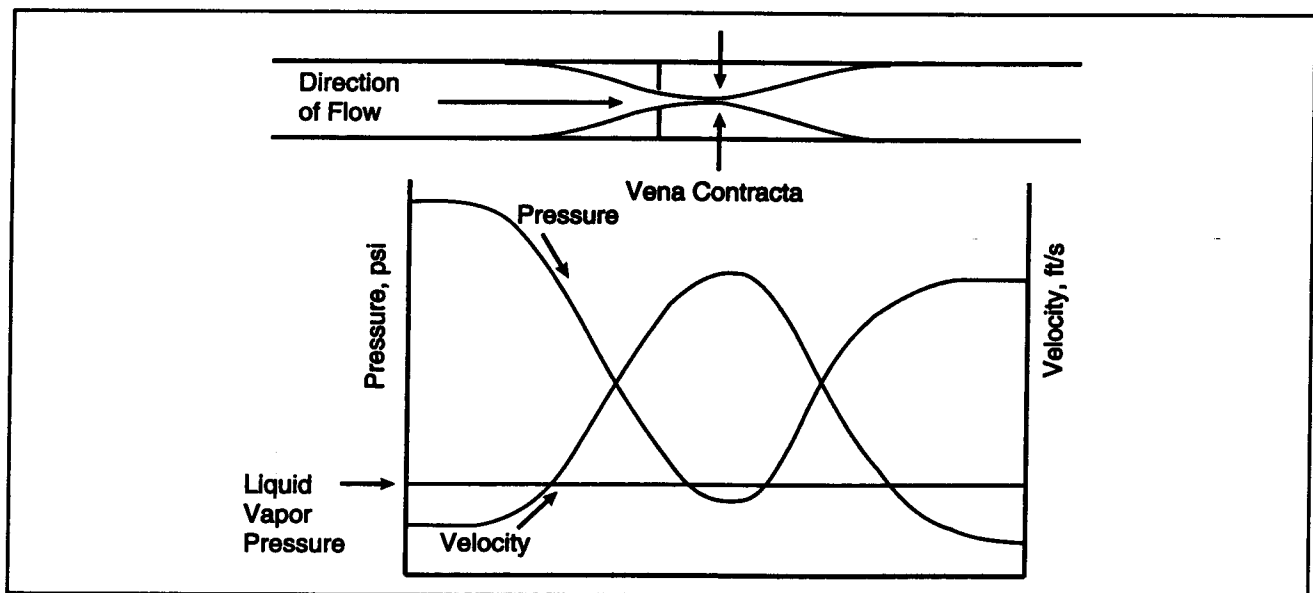


Figure 4.11 Pressure and Velocity Profiles

This type of problem is a common occurrence in water injection systems where a portion of the output from high pressure injection pumps is bypassed through a control valve back to an atmospheric suction tank.

"Anti-cavitation" valves can be employed to prevent this problem.^(4.26) Valves of this type reduce the pressure in a series of staged pressure drops. This technique maintains the flowing pressure above the vapor pressure of the liquid, and vapor bubbles cannot form, thus preventing cavitation.

Abrir válvula de descarga (↑ NPSH). Aumentar elevación de la succión, reducir **Hydrogen Damage** *diámetro*

Hydrogen atoms are formed at cathodic areas on a steel surface during corrosion by acid gases as previously mentioned. In sweet, air-free systems, most of the hydrogen atoms combine on the metal surface to form hydrogen gas molecules which subsequently evolve from the metal surface into the water.

In sour systems, sulfide ions slow down the rate at which hydrogen atoms combine to form hydrogen gas molecules. This results in an increased number of hydrogen atoms on the metal surface, which provides the driving force for diffusion of hydrogen atoms into the steel. Hydrogen atoms are extremely small and can diffuse through most metals.

There are three types of damage which can be caused by the diffusion of atomic hydrogen into steel: Hydrogen Blistering, Sulfide Stress Cracking (SSC) and Hydrogen Induced Cracking (HIC)

Hydrogen Blistering

During sour corrosion, atomic hydrogen diffusing through steel can combine to form molecular hydrogen within structural defects such as voids, laminations, microcracks, or discontinuities around inclusions.^(4.27) Once molecular hydrogen has formed within a defect, it is trapped, because hydrogen gas molecules are too large to diffuse out through the metal lattice. As corrosion continues, hydrogen atoms continue to diffuse into the defect creating additional hydrogen molecules, thus increasing the pressure in the defect. Increased pressure causes growth and further separation of the flaw.

This process is illustrated in Figure 4.12. Corrosion is occurring on the upper surface of the metal, and three things are happening to the hydrogen atoms:

1. A portion are combining to form hydrogen gas molecules on the corroding surface.
2. Some atoms diffuse completely through the metal to combine on the external surface.

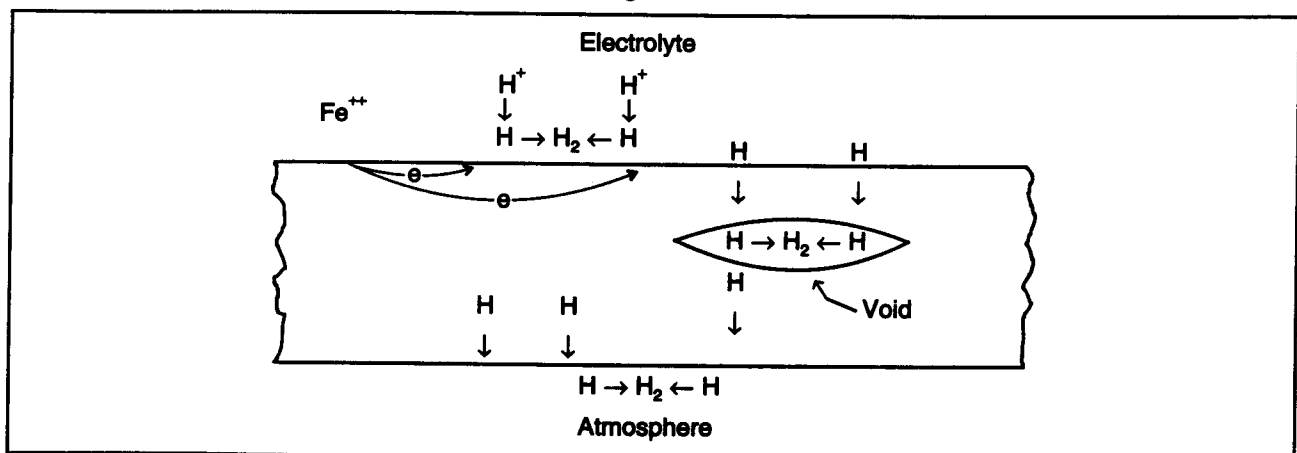


Figure 4.12 Illustration of the Mechanism of Hydrogen Blistering^(4.2)

3. Atoms diffuse into the void and form hydrogen gas there. The pressure created will eventually deform the metal and cause a blister.

Blistering is usually confined to the lower-strength grades of steel (70,000 to 80,000 psi tensile strength and a hardness of Rc 22 or less). Hardened or high-strength steels will normally crack rather than blister.

Hydrogen blistering is primarily a function of the steel "cleanliness," which is related to the impurities in the steel and the method of manufacture.

Hydrogen Induced Cracking (HIC)

Sometimes called "stepwise cracking" or "blister cracking," hydrogen induced cracking is a specialized case of hydrogen blistering which can occur during sour corrosion.^(4.28) HIC can occur when a steel contains numerous elongated defects which are parallel to the metal surface. Hydrogen can gather along the defects and create miniature blisters or cracks.^(4.29) Cracks on one plane tend to link up with cracks on adjacent planes to form "steps" across the thickness as shown in Figure 4.13. The cracks can reduce the effective wall thickness until the pipe is over-stressed and ruptures. Cracking is sometimes accompanied by surface blistering.

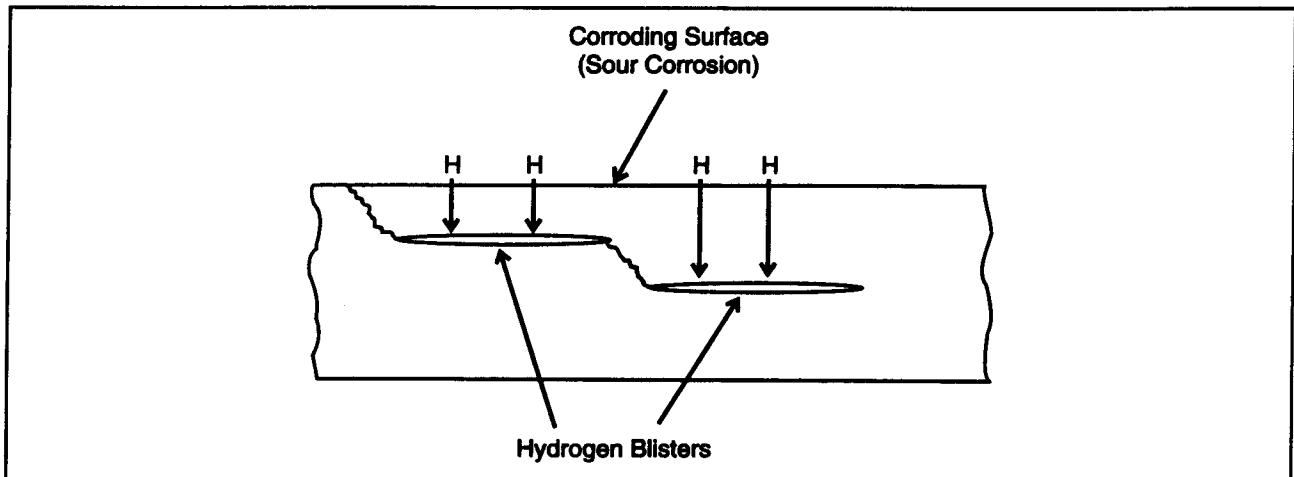


Figure 4.13 Schematic Representation of Hydrogen Induced Cracking

Sulfide Stress Cracking

Hydrogen embrittlement is the brittle failure of metallic materials at stress levels below their yield strength as a result of exposure to atomic hydrogen. Sulfide stress cracking (SSC) is a particular form of hydrogen embrittlement which occurs because of the entry of atomic hydrogen into steel as a result of sour corrosion. The exact mechanism by which the hydrogen causes a loss of ductility is a matter of technical debate.^(4.30)

In order for sulfide stress cracking to occur, all of the following are required:

1. Hydrogen sulfide
2. Water. Even a trace amount of moisture is sufficient.
3. A "high strength" steel. The exact strength level varies with the composition and micro-structure of the steel. (Although other materials are susceptible to sulfide cracking, we will confine this discussion to steel.)
4. The steel must be under tensile stress or loading. The stress may be residual or applied.

If all of these conditions are present, sulfide cracking may occur after some period of time. It is important to realize that sulfide cracking usually does not occur immediately after exposure to the sour environment but may take place after hours, days, or years of service.^(4.31) The susceptibility of a material to failure by this mechanism is primarily determined by the variables discussed in the following paragraphs.

Yield Strength or Hardness

"Plain" carbon steels with yield strengths below 90 000-100 000 psi [620 000-690 000 kPa] are generally considered to be immune to sulfide cracking. This corresponds to a hardness of about Rc 22. Strengths above this level are susceptible to cracking. The higher the strength, the shorter the time to failure. This is illustrated in Figure 4.14 which shows a correlation of failure time with hardness and applied stress for carbon steel exposed to 3000 ppm H₂S in water containing 5% NaCl.

If steel is alloyed with other materials, such as nickel, failure can occur at hardness levels less than Rc 22. Conversely, certain heat treatments can raise the maximum permissible hardness level above this value.

Stress Level

The stress may be either residual or applied. The time to failure decreases as the stress level increases (Figure 4.14). In most cases the stress results from a tensile load or from the application of pressure, or both. However, residual stresses and hard spots can be created by welding, or by cold-working the material (cold bending, wrench marks, etc.).

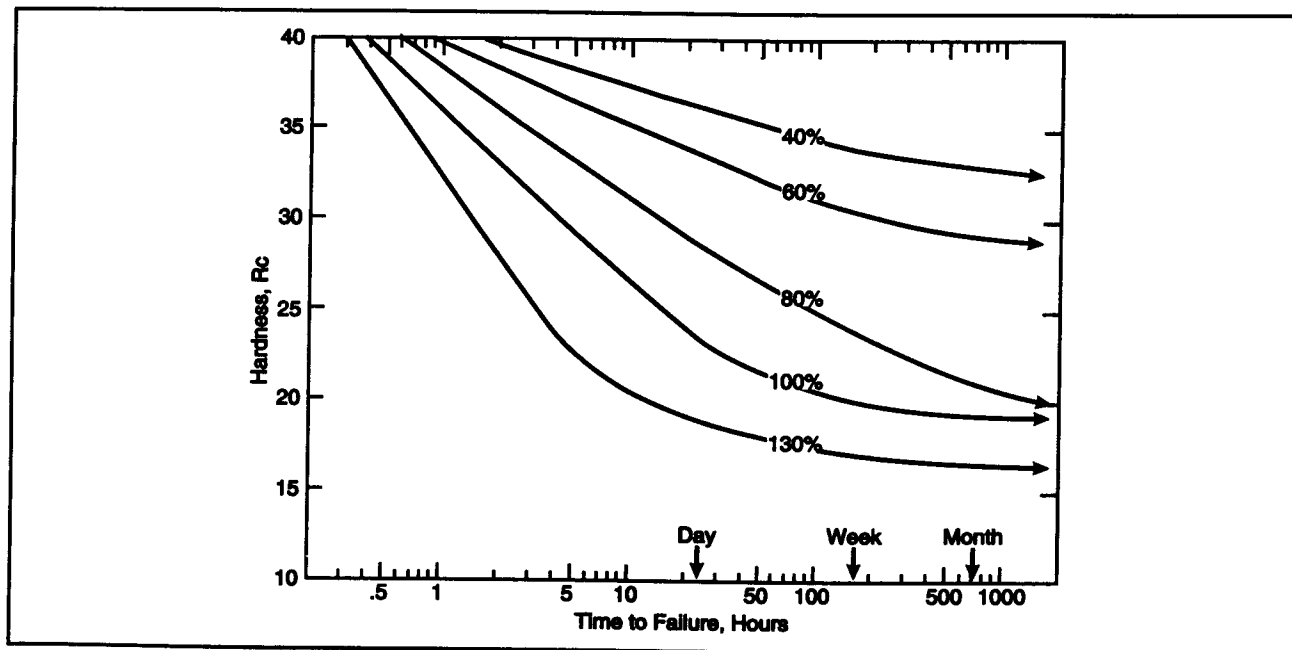


Figure 4.14 Failure Time as a Function of Hardness and Applied Stress^(4.32)

Hydrogen Sulfide Concentration

The time to failure increases as the H₂S concentration decreases. Figure 4.15 shows a correlation between failure time and hardness for carbon steel in 5% NaCl solution containing various concentrations of H₂S. Delayed failures can occur at very low concentrations of H₂S in water (0.1 ppm) and at

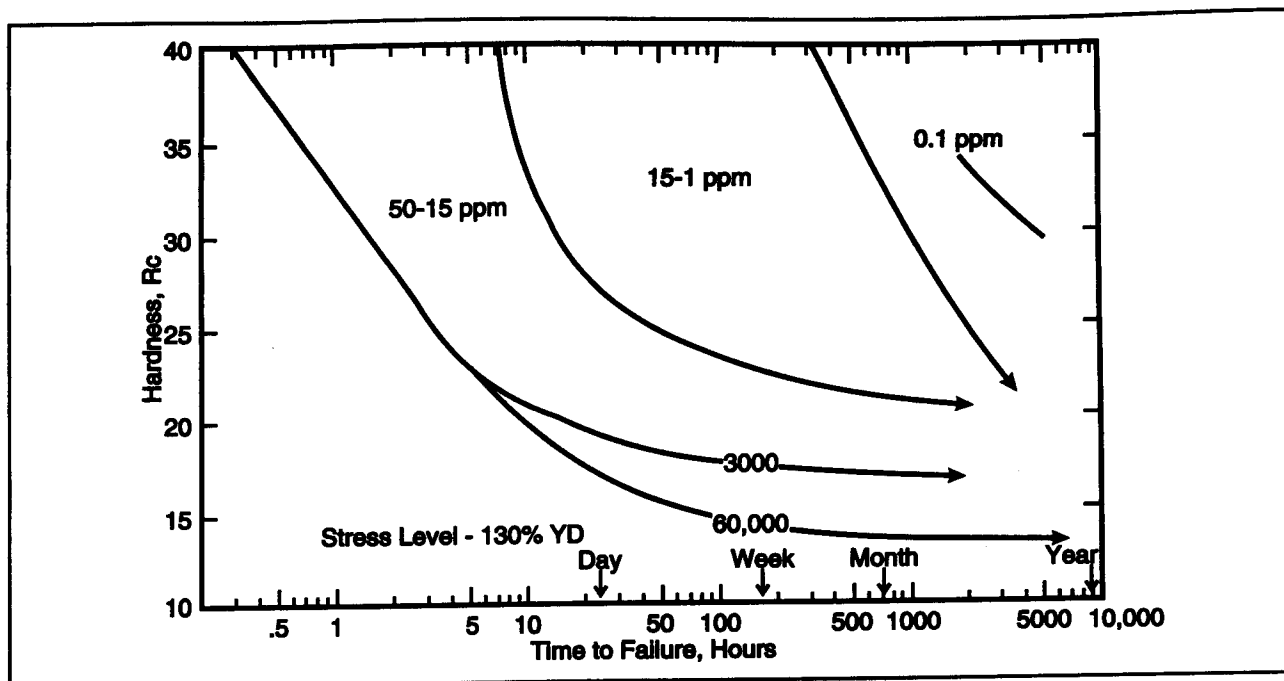


Figure 4.15 Correlation of Failure Time with Hardness and H₂S Concentration^(4.32)

partial pressures as low as 0.001 atmosphere [0.1 kPa] although the time to failure becomes very long.^(4.22,4.23)

pH of Solution

The cracking tendency of carbon steel increases as the pH decreases in H₂S containing brines as shown in Figure 4.16. Failures can be drastically reduced if the pH of the solution is maintained above 9.0.

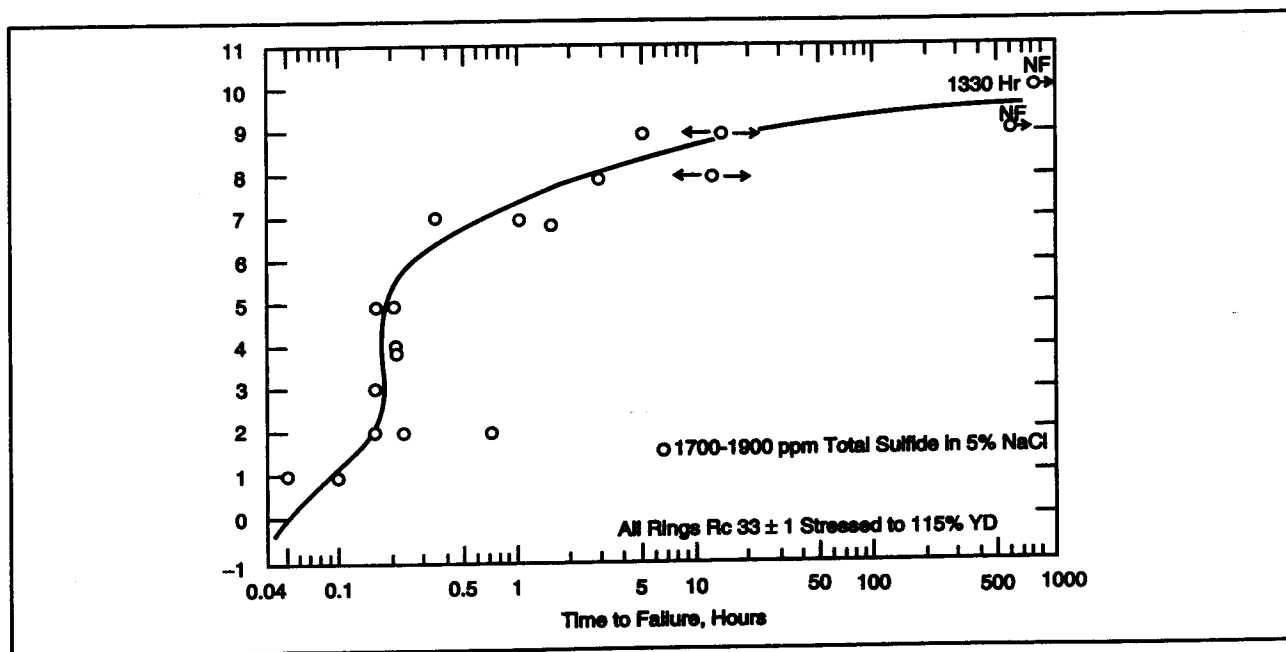


Figure 4.16 Correlation of Failure Time with pH^(4.32)

Temperature

The cracking susceptibility decreases as the temperature increases. This is illustrated for common grades of tubing and casing in Figure 4.17. Materials for application in environments containing H_2S should be selected according to NACE Standard MR0175 (latest revision), which is discussed later in this chapter.

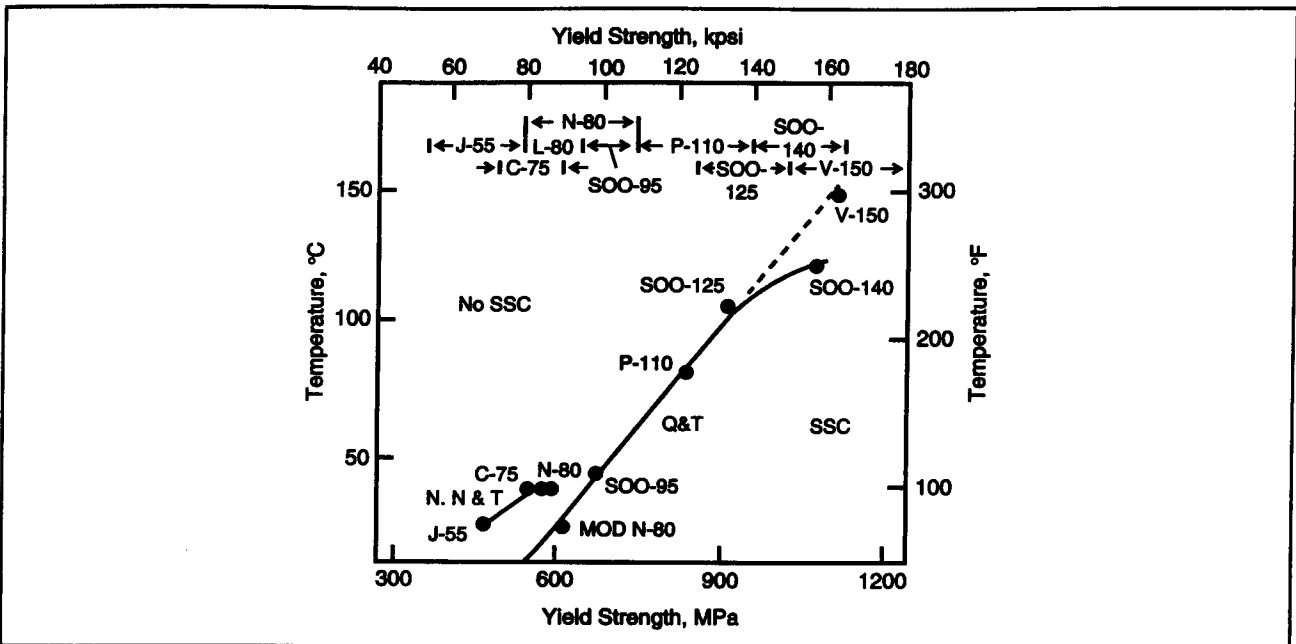


Figure 4.17 Effect of Temperature on Sulfide Stress Cracking Resistance^(4.33)

Corrosion Fatigue

This is the result of cyclic stress and corrosion. Most sucker rod breaks and drill pipe failures occur as a result of corrosion fatigue. It can also be the cause of pump failures. It is possible on any part that is subjected to a cyclic stress in a corrosive environment. It is a brittle failure which can occur at stress levels well below the yield strength.^(4.34)

Microbiologically Influenced Corrosion (MIC)

Corrosion can be caused by bacterial activity. Internal damage can result from bacterial activity in injection systems. External damage of buried structures can result from bacterial activity in soils. This subject is discussed in Chapter 5.

Fretting Corrosion

Fretting corrosion occurs when two metal surfaces are in contact with each other in a corrosive environment and are subjected to vibration or other relative motion. Accelerated attack results from the continuous removal of any protective films from the metal surfaces. It occurs mainly on machine parts such as ball and roller bearings, shafts and gears.

Electrolytic Corrosion

Electrolytic corrosion is quite similar to galvanic corrosion except that the direct current causing the corrosion originates from an external source. A typical example of electrolytic corrosion is the corrosion of foreign structures by stray currents from impressed current cathodic protection systems.

Chloride Stress Cracking

The 300 series stainless steels (such as 304 and 316) will crack in the presence of salt water at temperatures above 150°F [66°C] in the presence of applied or residual tensile stress.

Selective Leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes. Two commonly encountered examples are the selective removal of zinc in brass alloys (dezincification) and the selective removal of iron from gray cast iron (graphitization).

Dezincification

The commonly accepted mechanism consists of three steps: (1) the brass dissolves, (2) the zinc ions stay in solution, and (3) the copper plates out of solution and is redeposited as a spongy, porous replica of the original part. Examples of this type of corrosion have been observed in Admiralty brass exchanger tubes.

Graphitization

Gray cast irons are alloys of iron, carbon (2-4%) and silica (1-3%). The carbon exists as flakes of graphite within the metal. The graphite gives the metal a gray color on a fractured surface, hence the name gray cast iron.

When graphitization occurs, the iron or steel matrix is selectively dissolved, leaving the graphite network behind. Dimensional changes do not occur, but the cast iron loses strength and its mechanical properties, resulting in premature failure.

CORROSION CONTROL METHODS

Approaches to Corrosion Control

There are many methods of controlling or preventing corrosion in water handling systems. They can be classified into six general categories:

Alter Material Composition

A corrosion resistant alloy steel or a non-ferrous metal may be substituted for carbon steel, or plastic may be used. Corrosion resistant metals are more expensive than carbon steel. Plastic materials are usually subject to more severe pressure and temperature limitations than metal.

Alter Electrolyte Composition

The water composition may be altered by changing the pH, chemically or mechanically removing dissolved gases, or by mixing with another water. Other techniques are used, but these are most common in oilfield operations.

Physical Alteration of the System

Typical examples would include increase of NPSH to prevent cavitation, increased or decreased velocities by changing the diameter of tubular goods or line pipe, and institution of regular line pigging and vessel clean-out to reduce solids deposition.

Isolate the Metal from the Electrolyte

Plastic coatings and linings are very popular in tubular goods and tanks. Cement linings are frequently used in tubular goods.

Chemical Inhibitors

Chemical inhibitors can be viewed as a "coating," since most inhibitors used in injection systems are organic film forming materials.

Cathodic Protection

The application of sufficient electrical current to a metal immersed in water will stop corrosion. Current can be applied with sacrificial anodes or with impressed current if a source of power is available.

Method Selection

The selection of the method or combination of methods to be used in a particular application should be based on minimizing the cost of achieving the following objectives:

1. Obtain an acceptable service life for the equipment.
2. Prevent pollution of the environment.
3. Minimize the generation of suspended solids. This is especially important in water injection systems. Injection-wellbore plugging can be expensive.

Cost of Materials

The initial cost of materials, plus the cost of any additional materials required during the project life.

Labor Costs

Initial installation costs plus maintenance costs must be considered.

The Present Value of Money

Remember that the cost of expenditures to be made in future years must be discounted back to their present value to obtain the "true cost." Deferred dollars do cost less; however, the "put it off until tomorrow" philosophy can be dangerous. Both material and labor costs are rising rapidly and even deferred dollars can add up to a pile of cash. The tendency to defer investment has to be balanced

against the fact that it is often far cheaper to go ahead and spend the money on a good system in the beginning. If corrosion gets out of control, the remedy can be extremely expensive. On the other hand, it may be cheaper to let the system corrode and replace it when the time comes. This is seldom the case, however.

The severity and nature of any corrosion which may occur must be estimated during the design of the system so that adequate control measures can be instituted at the beginning. The system must then be monitored to measure the corrosiveness of the system so that the corrosion control program can be adjusted as necessary. The measurement of corrosion rates is extremely critical and will be covered later in this chapter.

CORROSION INHIBITORS

Corrosion inhibitors are selected for water systems in a variety of ways. Some of the more popular are:

- Wild guess
- Experience in the area
- Advice from chemical salesman
- Laboratory tests
- Field tests

Usually a combination of these techniques is employed. The following steps are recommended when an inhibitor must be selected:

1. Find out what is causing the corrosion. This is actually the first step in selecting any control method, and it is very important in selecting an inhibitor.

Determining the cause may involve determining the amount and kinds of dissolved gases present, or analyzing the corrosion product. The type of attack also must be determined.

2. Make an initial inhibitor selection with the help of technical personnel in your own company and in consultation with the chemical company of your choice. Major chemical companies maintain large technical staffs and can give you excellent advice on which of their products stands the best chance of working once you have defined the problem.

Initial chemical selection can also be made using laboratory or field tests. Good quality laboratory testing is difficult at best because of the difficulty of transporting fluids to the lab and running the tests without contaminating or changing the water in some way. However, comparative data can be generated using standard test waters.

Both linear polarization and potentiodynamic polarization^(4.35,4.36) methods, which are discussed later in this chapter, are extremely useful in selecting corrosion inhibitors for water injection systems. A portable side-stream apparatus can be used for initial chemical screening, as shown in Figure 4.18.

Water is flowed directly from the system through the test cell. Inhibitor is injected into the side-stream and the corrosivity of the inhibited water is monitored with one or both of the instruments.

The advantages of side-stream testing are many:

- Chemical evaluation is made on-site using uncontaminated water directly from the injection system.

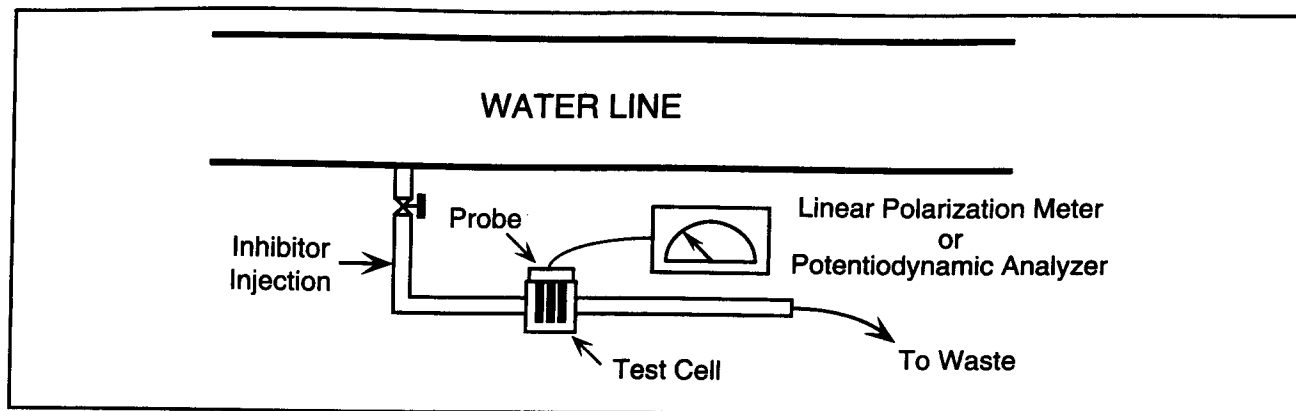


Figure 4.18 Side Stream Testing Setup

- Testing can be carried out quickly. Several inhibitors can be evaluated in a few days.
 - Linear polarization meters measure the instantaneous general corrosion rate. Changes in corrosion rate can be observed as they occur.
 - A portable potentiodynamic analyzer is the only monitoring tool available which permits rapid measurement of both the general corrosion rate and the pitting corrosion rate.
3. Once the initial chemical selection is made, field testing should then be carried out with diligent monitoring to determine how good a job you are doing. You may want to test one chemical or concentration in one part of the system and another in a different part of the system.

Once your final selection of inhibitor and concentration is made, monitoring must be continued. Systems can change in corrosivity with time.

Guidelines for Inhibitor Selection

Inhibitor Solubility

Water-soluble inhibitors are normally used in water systems.^(4.37) Water dispersible inhibitors may also be used and often afford better protection than the truly soluble inhibitors. However, there is usually concern over the possibility of "formation plugging" by inhibitors that are not completely soluble.

Dissolved Oxygen

"Normal" organic corrosion inhibitors do not effectively inhibit corrosion caused by dissolved oxygen. There are some organic corrosion inhibitors on the market which are somewhat effective against oxygen. However, these are not ordinary, garden-variety, organic inhibitors and are seldom as effective as normal corrosion inhibitors in the absence of dissolved oxygen.

Incompatibility

If other chemicals are being injected into the system (scale control, oxygen scavenger or bactericide), compatibility of the different chemicals should be checked. If they react with each other, their effectiveness may be reduced or destroyed.

Inhibitor Detergency

Most corrosion inhibitors possess "detergency" to help keep the system clean. This is desirable since the inhibitor must be able to reach the metal surface to do its job. If sludges accumulate on the surface, they can interfere with the inhibitor, so a certain amount of detergency is desirable to maintain a clean system. Problems can arise when inhibitor injection is first initiated into a water injection system if the inhibitor has too much detergency. Large quantities of solids can be loosened and formation plugging can result.

It is advisable to inspect surface facilities prior to initiating injection. If they are extremely dirty, it may be advisable to clean the system prior to starting inhibition. Otherwise, it is advisable to consider installation of cartridge filters at appropriate points to keep dislodged solids out of the formation. It is an operational headache until the system cleans up, since the cartridges must be changed frequently. However, it may be worth it in the long run if formation damage can be avoided.

Inhibitor Cost

Inhibitor cost is listed last to emphasize a very critical point. Never make an inhibitor selection based on which inhibitor costs the fewest dollars per gallon. Sometimes the most expensive inhibitor (\$/gal) will be the most effective (take fewer gallons) with the net result that the total cost of inhibition is lower than if a cheaper chemical is used.

Obviously, the most expensive inhibitor is not always the best. Inhibitor effectiveness can only be established by evaluation. The primary point to be made is that the "cheapest" inhibitor is often not the least expensive inhibitor.

Inhibitor Application

Organic inhibitors are supplied in liquid form and are injected with chemical pumps. The chemical is often diluted for ease of application. In cold climates the chemical must be winterized (usually with alcohol) or kept in a heated building. If it is to be winterized, the chemical must be compatible with alcohol. Alcohol will cause some inhibitors to precipitate from solution.

Inhibitors are injected into water systems on a continuous basis. A good inhibitor should be effective at a concentration of 5-25 ppm.

INTERNAL COATINGS AND LININGS FOR TUBULAR GOODS

Plastic Coatings

Types of Plastics

There are two basic types of plastics used for coatings and linings: thermoplastics and thermosetting plastics.

Thermoplastics become softer when heated, but they can then be cooled and regain their original physical properties. Of course, if they get too hot, the molecules may break down, but this is not a problem in normal applications. Examples of thermoplastics are PVC and polyethylene.

Thermosetting plastics become harder and more brittle as they are heated. Cooling will not restore them to their original state. Examples of thermosetting plastics are phenolics and epoxies.

Coating Thickness

Plastic coatings are also classified according to thickness. Coatings with a thickness of 5-9 mils [127-178 μm] are classified as thin-film, while coatings in excess of 9 mils [178 μm] are usually called thick-film coatings.

Thick-film coatings are typically recommended for water injection service, although thin-film coatings are also in common use. The reason is that it is much easier to achieve a 100% holiday-free coating with the thick-film materials and most vendors will guarantee thick-film coatings to be holiday-free.

In contrast, the specification for standard **thin-film** coatings quoted by most vendors is that a minimum of 85-90% of the lengths in a given order (depending on range and diameter) will be holiday-free. The remaining lengths can contain 5-9 holidays each, again depending on pipe size.

Holiday-free thin-film coatings can be obtained at a premium — usually about 10% over the list price for the coating. However, the extra cost is a small price to pay for the increased quality and can be justified in most cases.

Coatings are applied in two ways:

- Liquid Applied Coatings

Most coatings are applied as a liquid in a series of thin coats to achieve the desired thickness, and then baked.

- Fusion Bonded Coatings

This type of coating is applied as a powder to a heated pipe, which bonds and cures the coating simultaneously. A popular example is fused epoxy.

Some typical examples of coatings currently recommended for water injection service are given in Table 4.4.

TABLE 4.4
Internal Coatings for Water Injection Service

Type	Thickness		Max Temp	
	mils	mm	°F	°C
Epoxy-polyamide	12-20	0.3-0.5	150	66
Fused Epoxy	10-20	0.25-0.5	250	121
Modified epoxy	8-15	0.2-0.4	300	149
Epoxy-phenolic	5-9	0.13-0.23	250	121
Phenolic	5-9	0.13-0.23	400	204
Nylon	10-30	0.25-0.76	225+	107+

Pipe Preparation

Pipe or tubing is usually pickled to remove mill scale and acid soluble material, then either sand or flintblasted to white metal. This is an extremely critical step. If the surface preparation is poor, disbonding and subsequent coating failure is likely.

Coating Inspection

The coating should be visually inspected between coats, and the final cured film thickness measured. It should then be "holiday checked." This is accomplished by applying an A-C potential of about 2500 volts across the coating with either a wet sponge or a dry spark for thick-film coatings. A 67.5 volt D-C potential with a wet sponge is used for thin-film coating inspection. If there is a thin spot in the coating, or if the coating is missing in spots, current will flow through the thin or bare spot and an alarm will sound. The joint should be rejected.

If you are really concerned about quality control, you should hire an independent inspector to assure quality control. This is not to infer that coating companies will intentionally do a poor job. Quite to the contrary, they usually do a very good job. But if the application is really critical, it is in your own best interest to double check.

Tubing Couplings

One of the most critical areas for coating in tubing is the pin end, around to the threads, and the exposed section of the coupling. A number of systems are available to eliminate or reduce holidays in this area, including various types of rubber and plastic compression rings.^(4.38)

Pipe Connections

There are a number of systems available for joining internally coated line pipe.

Threaded Pipe

Internally coated threaded line pipe is used primarily in small systems where fittings are used such as at injection well tie-ins.^(4.39) It is also used for tie-ins on fiberglass injection systems.

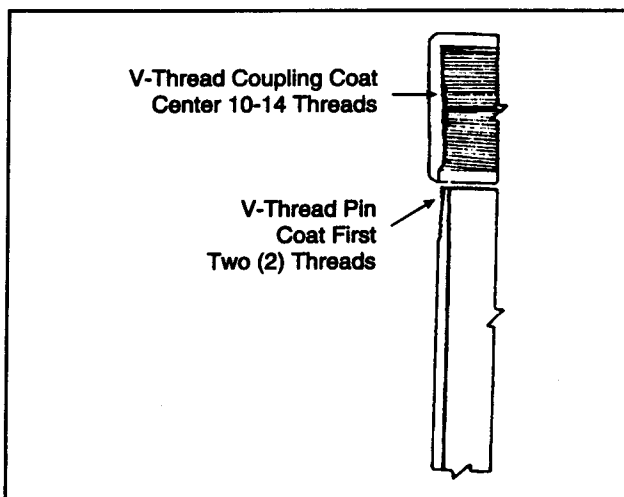


Figure 4.19 Coating Detail for Threaded Line Pipe Connection^(4.39)

Externally Grooved Connection

This connection can be used for low pressure injection lines. Non-metallic seals are used in a clamp to connect this joint. Seals that allow the ends of the coated pipe to seal against the rubber should be used.^(4.39)

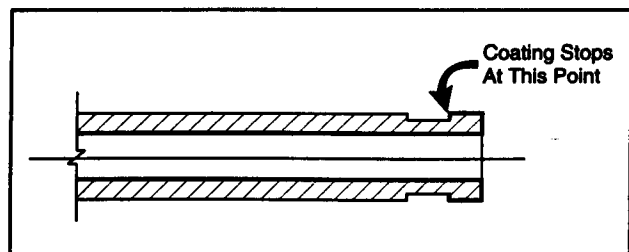


Figure 4.20 Coating Detail for Grooved Connection^(4.39)

Flanged Connections

Flanged connections can be used for high pressure tie-ins. The flanged sections should be prefabricated and shop coated if possible.

Weldable Couplings

Proprietary weldable couplings such as the AMF Thru-Kote¹ or the Flexweight Perma-Couple² are in common use.

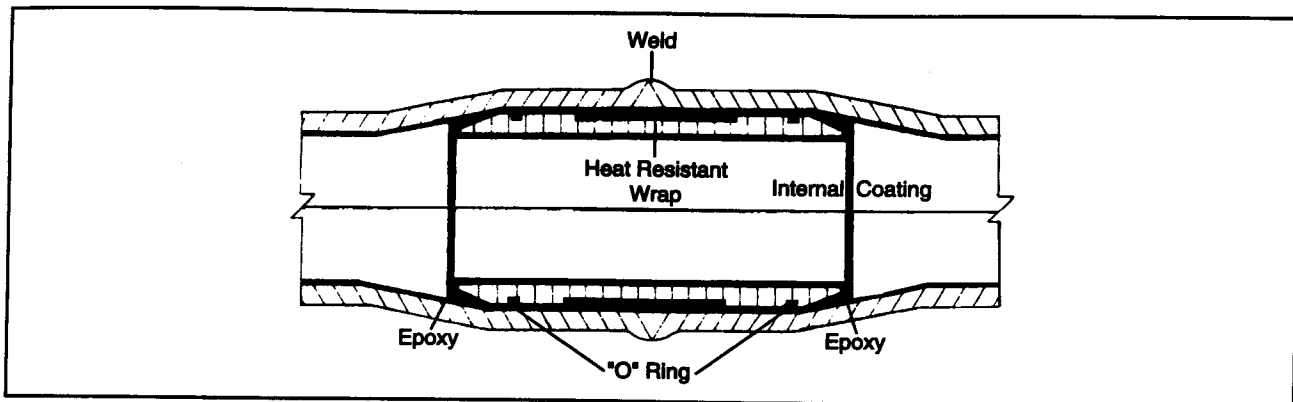


Figure 4.21 Schematic of Thru-Kote Joint

The Thru-Kote system utilizes mechanically belled pipe and an internal metal sleeve machined from sections of pipe. The sleeve is internally coated, and is wrapped with a heat-resistant material to prevent damage to the coating during the welding process. O-rings prevent welding gas damage to the epoxy sealant which is used to seal the sleeves to the bell-joint annulus and provide a smooth contour to eliminate turbulence. A similar connection for unbelled coated line pipe is also available.

The Perma-Couple system utilizes retainer rings which are welded onto the outside of the pipe prior to internal coating. The steel coupling contains a one-piece, molded elastomeric liner bonded permanently to the ID of the coupling. Joints are formed by hydraulically pressing pipe into each end of the coupling to create a seal against the shoulder of the seal. The coupling is then welded to the retainer rings. Heat shields are used to prevent damage to the internal coating during welding.

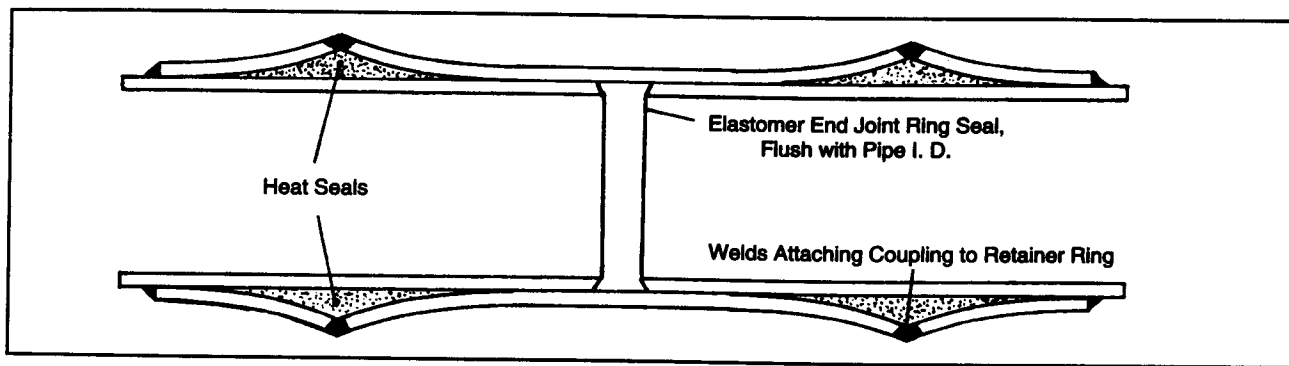


Figure 4.22 Schematic of Perma-Couple Joint

¹ Thru-Kote[®] is a registered service mark of AMF Tuboscope, Inc., Houston, TX.

² Perma-Couple[™] is a registered trade mark of Flexweight Corporation, Great Bend, KS.

Mechanical Interference Fit Connections

Proprietary mechanical connections which eliminate the welding process are also in common use. There are two basic types of joining systems: bell and pin joints, such as Zap-Lok^{3(4.40)} and Crimp-Kote^{4(4.40)}, and external sleeve joining systems like the Positive Seal coupling.⁵

In the Zap-Lok system, shown in Figure 4.23, the ends of each joint of line pipe are specially modified by cold working to create the joint surfaces. The bell end is expanded to a diameter slightly less than the outside diameter of the pipe. The pin end has a groove rolled in the circumference with the end swedged slightly inward to allow insertion into the belled end.

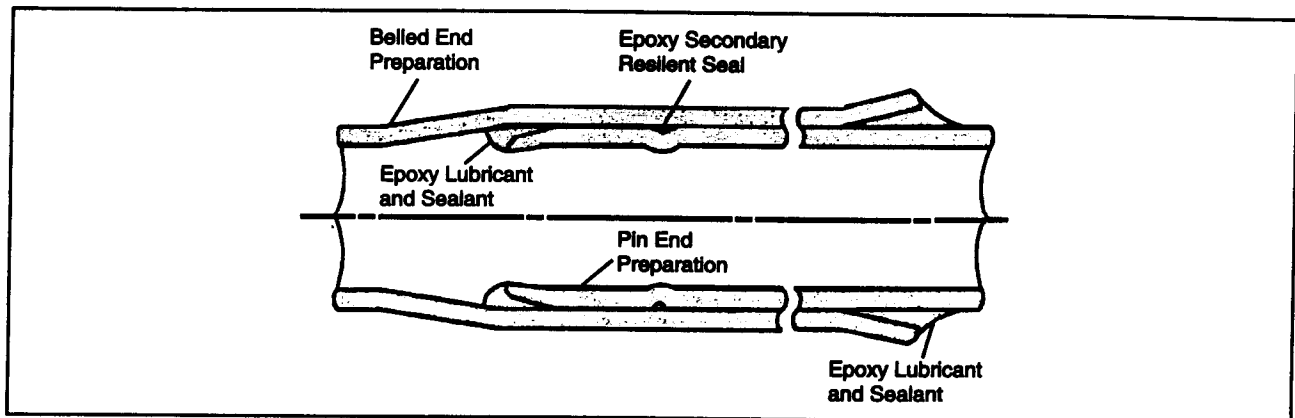


Figure 4.23 Schematic of Zap-Lok Joint

Epoxy resin is applied to the bell and pin of each joint and the two ends are forced together using a portable hydraulic press, resulting in a controlled interference fit. The epoxy serves both as a sealant and as a lubricant to aid in making up the connection.

The Positive Seal coupling system (Figure 4.24) utilizes an external coupling with serrated threads on the internal coupling surface. No special end preparation of the pipe is required, other than a conventional welding bevel.

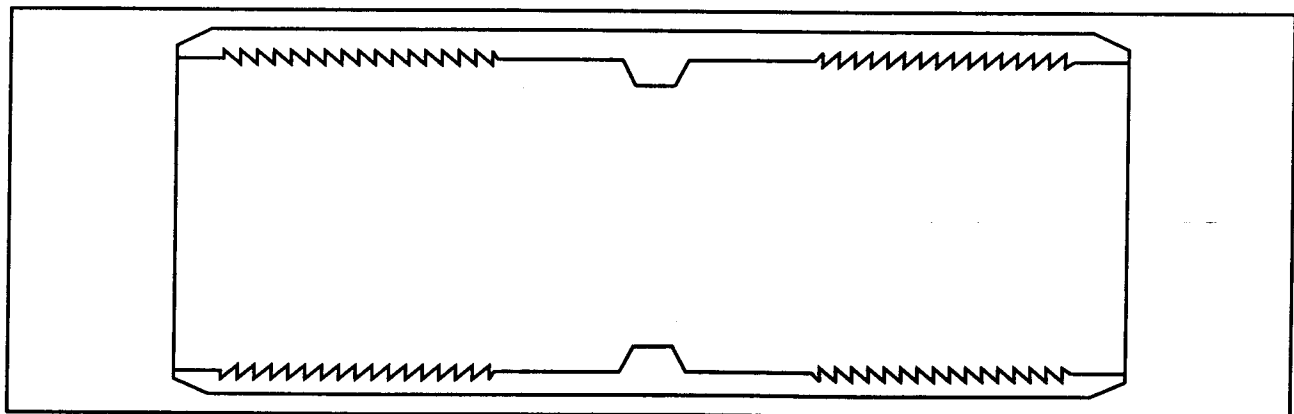


Figure 4.24 Positive Seal Coupling

3 Zap-Lok[®] is a registered service mark of PA Incorporated, Houston, TX.

4 Crimp-Kote[®] is a registered service mark of AMF Tuboscope, Inc., Houston, TX.

5 Positive Seal[®] is a registered service mark of Jet Air International, Inc., Houston, TX.

Before the pipe ends are inserted into the coupling, an epoxy sealant is applied to the exterior surface of the pipe ends and to the interior surface of the coupling. The pipe is then pressed into the coupling with a hydraulic ram until the weld bevel makes contact with the shoulders in the coupling. The epoxy prevents metal galling during coupling installation and cures to form a seal around the pin ends.

Field Coating of Weld Area

In pipe diameters greater than 6 inches, it is possible to weld internally-coated pipe in a normal manner, and then abrasive blast the weld area and coat it with a fusion bonded epoxy in the field. The abrasive blasting and coating is done by a special crawler machine.^(4.41)

Handling Plastic Coated Pipe

One of the many keys to successful service from internally coated tubular goods is careful handling during installation. If you have done a perfect coating job and then damage the coating during installation, you have just assured premature failure.

Some handling recommendations:

1. Don't use hooks or metal bars inside the ends of the pipe when unloading.
2. Don't run metal rabbits.
3. Leave the thread protectors on the pipe until you are ready to stab it. Use a stabbing guide if possible.
4. Don't run wire line tools in coated tubing unless you absolutely have to.

Cement Linings^(4.42-4.45)

Cement-lined tubing and line pipe is widely used in injection systems. The most widely used lining composition consists of Portland cement and sand. The pipe is lined by a centrifugal casting method to an average thickness of 1/4-3/8" (6.35-9.5 mm) depending on pipe size.

The Portland cement used should contain less than 3% tricalcium aluminate so that it will be resistant to attack by any sulfate ions in the water. Reaction between tricalcium aluminate and sulfate ions causes the cement to swell and crack. ASTM Type III or API Class B cements are resistant to sulfate attack.

Advantages of Cement Linings

1. Low cost.
2. They can be applied to new or used tubular goods.
3. A certain amount of cracking can be tolerated without loss of corrosion protection. The pH at the base of the crack (the pipe wall) is usually high enough to prevent appreciable attack. However, corrosion can occur under some conditions.

Disadvantages of Cement Linings

1. Cement linings add weight and reduce the I.D. of the pipe.
2. It is not advisable to acidize through cement lined tubular goods. Acid dissolves cement.

3. It is difficult to get a good welded joint. Several methods have been used with varying degrees of success. Asbestos gaskets and hydraulic cements have been very popular. The gaskets have apparently been most successful.
4. Excessive pressure surging can cause extensive cracking, and even failure.

Handling Practices

1. Don't bend cement-lined pipe unless you have to. Suggested minimum bend radii are shown in Table 4.5. For sharp bends, use cement lined fittings.
2. Be careful during loading and unloading. Don't drop the pipe, pick it up by the ends and let it sag in the middle, or run over it with a truck. Avoid impact loads.
3. Apply the same general handling practices as suggested for plastic coated tubing.

TABLE 4.5
Minimum Bend Radii for Cement Lined Pipe

Pipe Diameter (in.)	Minimum Bend Radius (ft.)
2 3/8	150
3 1/2	220
4 1/2	275
6 5/8	300
8 5/8	485
10 3/4	575

Plastic Liners

Plastic pipe can be inserted into steel pipe or tubing to provide internal corrosion protection. Three basic types of lining systems are presently in common use in oilfield operations:

Grouted Liners

Plastic pipe is inserted into individual joints of tubing or line pipe, and Portland cement is pumped into the annular space between the two pieces of pipe. Typical liners include polyvinylchloride (PVC) and glass fiber reinforced epoxy (FRE). The PVC is recommended for application up to about 160°F [71°C] while the FRE is usually selected for temperature in excess of 160°F [71°C] up to a maximum of about 250°F [121°C].

Longer lengths of plastic pipe are inserted into pipelines and grouted in place with Portland cement. Thermoplastics such as PVC or polyethylene in lengths of 2000-3000 ft are commonly used. This procedure is usually employed to repair badly corroded lines. Shorter lengths of fiberglass pipe have also been used as liners. The glass fibers reinforce the composite fiberglass/grout/steel system and increase its burst pressure.^(4.46)

Expanded Liners

Although several plastics have been used, liners manufactured from ultra high molecular weight, high-density polyethylene (UHMWHDPE) plastic with much higher toughness and ductility than conventional extruded polyethylenes is widely used in pipelines.^(4.46-4.49) The liner is inserted into the

pipeline in lengths that normally range from 2500 to 5000 ft, and the lined sections are connected with special flanges. The liner is then pressurized to expand the plastic liner until it compressively sets against the internal wall of the steel line. The maximum operating temperature is said to be approximately 180°F [82°C].

Bonded Liners

Line pipe or tubing can be lined with polyvinylchloride (PVC) which is bonded to the pipe with a thermoset bonding agent. The bonding agent is applied to the internal tubing surface and to the external surface of the PVC liner, and allowed to dry. The liner is then inserted into the pipe, heated, and pressurized. The heat-softened plastic expands and bonds to the inner wall of the tubing. Regular line pipe can also be lined and joined with a mechanical interference joint as shown in Figure 4.25.

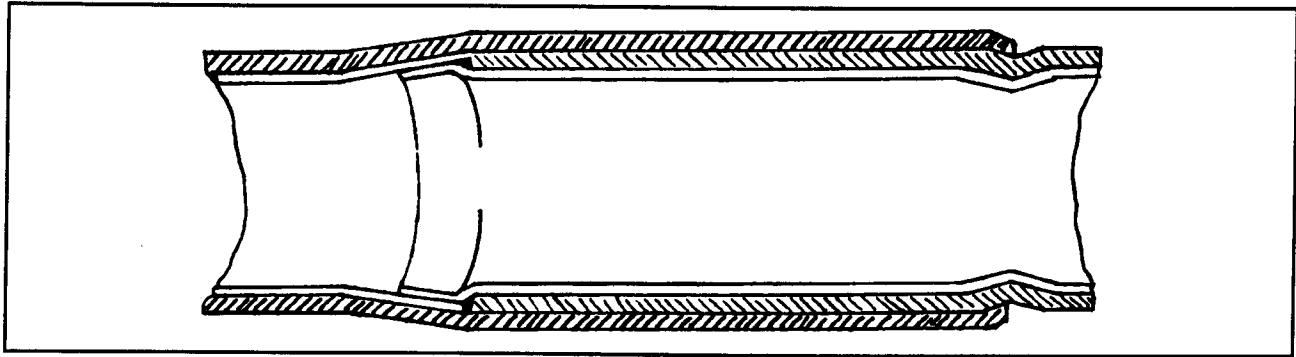


Figure 4.25 Mechanical Interference Joining of Lined Pipe (Courtesy Salta Pipe Co., Inc.)

INTERNAL VESSEL COATINGS AND CATHODIC PROTECTION

Coating of Water Storage Tanks and Other Vessels

It is generally advisable to completely coat the internal surface of water storage tanks to protect against corrosion in three areas:

1. The underside of the roof and the walls above the water line. Only a coating can protect this area against corrosion resulting from condensation of water vapor. In water storage tanks, corrosion in this area is frequently aggravated by oxygen entry.
2. The tank walls below the water line. Corrosion inhibitors can control attack in this area; however, coating is recommended if the remainder of the tank is coated.
3. The tank bottom. Due to the frequent occurrence of deposits on tank bottoms, it is a favorite location for bacterial growth and under-deposit corrosion. Biocides or corrosion inhibitors are seldom effective in this situation because they are shielded from the metal surface.

If possible, small tanks should be coated in a coating plant or at the fabrication yard. Better control can be exercised over surface preparation and coating operations, and the results are usually better than a field coating job.

Filters should also be coated, and deaerators *must* be coated. Coating application should be carried out in a shop.

Field Application

If a tank must be coated in the field after it has already been in service, adequate surface preparation is the biggest obstacle to a successful coating job. All grease or oil should be removed from the surface with solvents. The surface should then be dry sandblasted to bright metal, or machine cleaned with wire brushes. All dust should then be removed from the surface by blowing with dry air or use of an industrial vacuum cleaner. The first coat should then be applied immediately before the surface rusts or is contaminated in some other way. Never finish the surface preparation and then wait until the next morning to start the coating operation. Application in high humidity should be avoided if at all possible.

Rigorous inspection during both the surface preparation and the actual coating job is highly recommended.

Coating Selection

There are many coatings available which can be used for internal tank coatings. Although the most widely used oilfield tank coatings have historically been the coal tar epoxies, other widely used coatings include the epoxy, epoxy-phenolic, and flake-filled polyester coatings.^(4.50,4.51)

Flake-filled polyester coatings have been used very successfully for internal coating of filters, deaerators, and other vessels handling aerated seawater.

Cathodic Protection

It is almost impossible to get a perfect coating job. There will always be a few imperfections, or "holidays," and corrosion at these points can lead to coating failure. Therefore, it is strongly recommended that cathodic protection be applied in conjunction with vessel coatings. The cost of cathodic protection will usually be about 10% of the cost of the coating job.

Principle

Earlier in this chapter it was pointed out that metal loss occurs at anodic areas on steel. These are areas where current is leaving the metal surface to flow through the electrolyte to the cathodic areas. When current leaves a metal surface it takes metal with it.

The principle of cathodic protection is to convert the whole metal surface into a cathode. This is accomplished by forcing sufficient current to flow to the structure to be protected so that there is no net flow of current from any point on the metal surface.

When external current is applied to a corroding surface, part of it goes to the anodic areas and part of it goes to the cathodic areas as shown in Figure 4.26.

The secret to success is to apply sufficient current to the structure so that $i_{pa} \geq i_a$. In other words, there must be enough current going to the anodic areas to "cancel out" the natural corrosion current. There must be no net current leaving the surface if corrosion is to be stopped.

Current Sources

Galvanic Anodes

Galvanic anodes are made of special high purity alloys of magnesium, aluminum, or zinc. All of these materials are more active (eager to corrode) than steel in most soils and waters. Therefore, if we

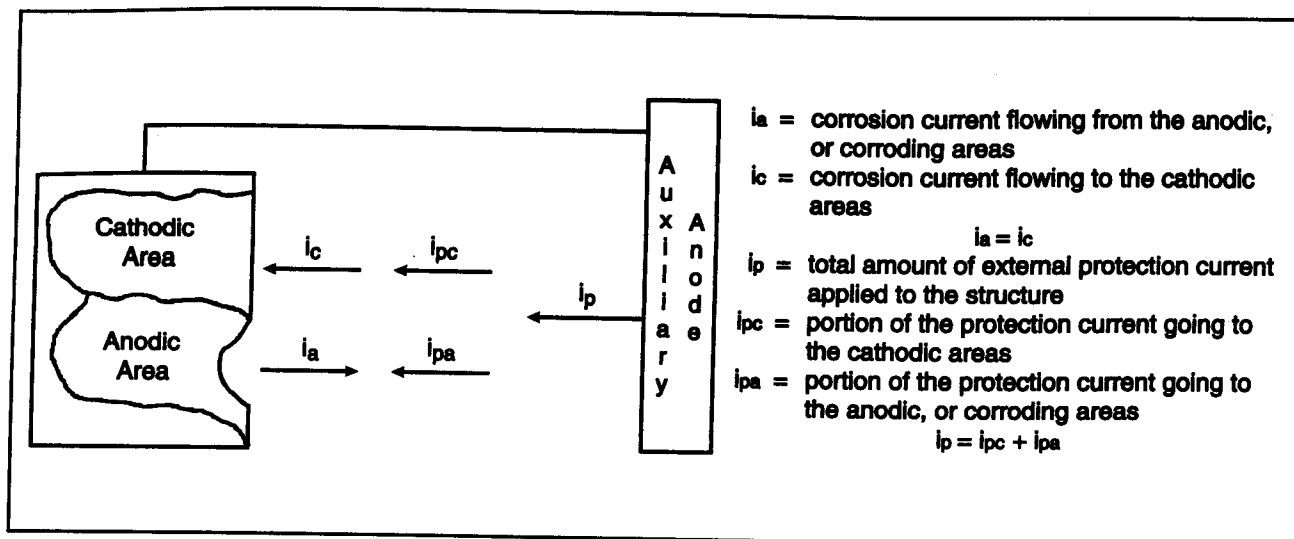


Figure 4.26 Illustration of Cathodic Protection

connect one of these more active metals to a piece of steel and immerse them in the same electrolyte, the more active metal will tend to corrode (become the anode) and the steel will stop corroding (become the cathode) as shown in Figure 4.27.

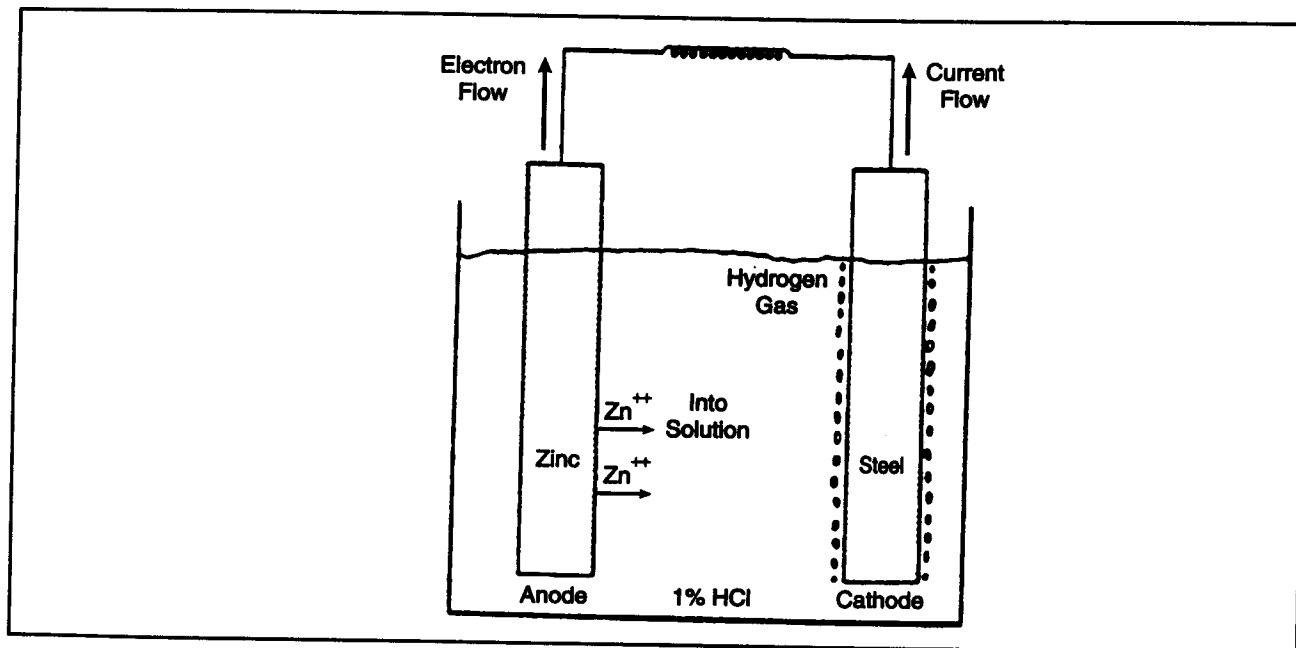


Figure 4.27 Galvanic Cell

A summary of the properties of anode materials commonly used in water is given in Table 4.6.

Magnesium

Magnesium anodes have the highest driving potential of the common sacrificial anode materials, making it the choice for soils and high-resistance waters. It is often necessary to use an external resistance to obtain reasonable anode life in brines.

TABLE 4.6

Energy Capabilities and Consumption Rates of Galvanic Alloys in Seawater^(4.54)

Galvanic Anode Alloy	Energy Capability (amp-hr/lb)	Consumption Rate (lb/amp-yr)	Potential (-volts*)
Aluminum-Zinc-Mercury	1250-1290	7.0-6.8	1.0-1.05
Aluminum-Zinc-Indium	1040-1180	8.4-7.4	1.05-1.10
Aluminum-Zinc-Tin	420-1180	20.8-7.4	1.0-1.05
Zinc (MIL-A-18001H)	354-370	24.8-23.7	1.0-1.05
Magnesium (H-1 Alloy)	500	17.5	1.4-1.6
* Reference Electrode: Ag/AgCl			

Zinc

Zinc can only be used in low resistivity soils and waters. The most commonly used zinc alloy, ASTM B418-80 Type 1, should be restricted to temperatures below 120°F [50°C].^(4.52) At temperatures above about 150°F [66°C], zinc and steel tend to reverse polarity. The steel becomes the anode and corrodes in preference to the zinc.

Aluminum

Aluminum is the preferred anode material for most oilfield brine systems because it has a high current capacity relative to zinc and magnesium. However, the current capacity begins to decrease at about 130°F [55°C], falling from 1100-1200 amp-hr/lb to values as low as 440 amp-hr/lb at a temperature of 165°F [75°C], depending on anode composition.^(4.53)

Impressed Current Systems

DC current can also be applied through an inert anode such as graphite if power is readily available. A rectifier is necessary to convert AC current to DC current.

Criteria for Cathodic Protection

The most important criterion for protection is to supply sufficient current to the vessel to achieve a vessel-to-water potential of -0.85 volts with respect to a Cu/CuSO₄ half-cell, or -0.80 volts with respect to a Ag/AgCl reference electrode.

Current densities (the total amount of current applied divided by the area to which the current is applied) are often used as design criteria. Commonly used rules of thumb are:

Coated Vessels:

$$0.5 - 2.0 \text{ mA/ft}^2 \quad [5 - 22 \text{ mA/m}^2]$$

Uncoated Vessels:

$$5.0 - 10.0 \text{ mA/ft}^2 \quad [54 - 108 \text{ mA/m}^2]$$

Where: 1 mA = 1/1000 ampere

There is a considerable range in requirements due to differences in water composition and conductivity. Potential measurements should be used to determine if protection is being achieved. Over-protection (too much current) can cause coating disbonding.

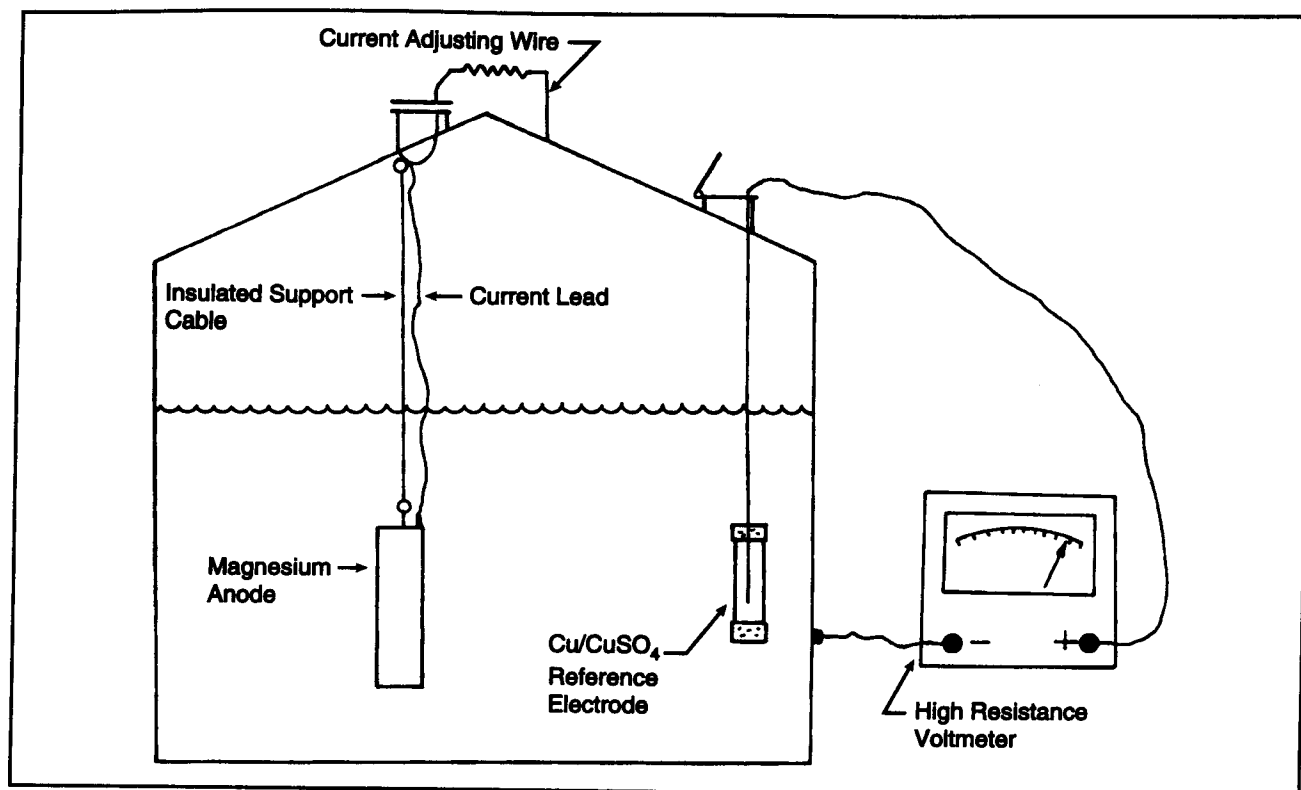


Figure 4.28 Cathodic Protection of a Water Storage Tank

It is also important that the anode (or anodes) be uniformly distributed within the tank to give uniform current distribution. The anodes should not be allowed to lay on the bottom of the vessel or to touch its sides.^(4.55)

Cathodic protection is a rather complex art and you should enlist the aid of your own company cathodic protection expert or a good supplier to help you with the details of an installation. You should then learn how to monitor performance by taking current and potential readings to ensure success.

NON-METALLIC TUBULAR GOODS

Types

There are three types of non-metallic tubular goods in common use in oilfield systems^(4.56)

Extruded Thermoplastic Pipe

Typical examples suitable for water service are:

1. Polyvinylchloride (PVC)
2. Chlorinated Polyvinylchloride (CPVC)
3. Polyethylene
4. Polypropylene
5. Acrylonitrile-Butadiene-Styrene (ABS)

Of these, PVC is probably the most widely used.

Glass Fiber Reinforced Thermoset Pipe (FRP)

There are two major classes in common usage:

- Fiberglass reinforced epoxy
- Fiberglass reinforced polyester

The reinforced epoxy is most commonly used in the oilfield. It is the strongest of the non-metallic tubular goods, and the most expensive. It has one peculiarity which is not found in other non-metallic piping. It will "weep" before it will fracture or burst. (Weeping is the seeping of fluid through the pipe walls by flowing along the glass fibers until it reaches the outer pipe surface.) Because of its strength and relatively high temperature rating (up to 300°F), fiberglass reinforced epoxy has been used for high pressure water injection systems and for tubing in injection and disposal wells. This type of pipe is made by applying epoxy to glass filaments which are wound around a removable mandrel or by a centrifugal casting process.

Fiber reinforced pipe should be purchased to API Specifications:

- API 15LR Low Pressure Linepipe (< 1000 psi)
- API 15HR High Pressure Linepipe (> 1000 psi)

Cement-Asbestos

This is the oldest of the three. It is made of Portland cement, asbestos fibers and silica. It has a maximum working pressure of about 150 psi [1035 kPa].^(4.57) It is also relatively fragile and must be handled carefully to avoid breakage.

Joining Methods

The methods used to join common types of non-metallic piping are summarized in Table 4.7.

TABLE 4.7
Joining Methods for Non-Metallic Pipe

Material	Joining Methods		
	Heat	Solvent	Thread
Thermoplastics			
PVC		x	x
CPVC		x	x
Polyethylene	x		x
Polypropylene	x		x
ABS	x	x	x
Thermosetting			
Fiberglass Reinforced Epoxy		x	x
Fiberglass Reinforced Polyester		x	
Cement-Asbestos*			x

* A rubber ring seal is also used.

Heat Welding

A heating element is used to soften the ends of the joints which are then butted together and held in position until the joint cools. A slight amount of upsetting occurs.

Solvent Welding

Solvent is applied to both the pin and collar ends, then glue is applied over the solvent. The joints are quickly pushed together allowing the pin end to fuse inside the collar.

Threaded Joints

Threaded joints can be used where the wall thickness is sufficient. In threaded and coupled thermoplastic pipe the working pressure rating is reduced by 50%. Threads in fiberglass reinforced epoxy pipe are either cut in an upset end or molded onto the standard pipe so there is no reduction in wall thickness.

Advantages of Non-Metallic Piping

1. Non-metallic materials are immune to corrosion by water.
2. They are light weight, resulting in lower freight costs and easy handling.
3. Non-metallic pipe is quickly and easily joined and installed.
4. No external corrosion protection, such as coating, wrapping, or cathodic protection, is required.
5. The smooth internal surface results in lower fluid friction loss.

Disadvantages of Non-Metallic Piping

1. Non-metallic pipe has rather low working temperature and pressure limits.
2. These limits are difficult to predict with assurance. The pressure and temperature limitations are often interrelated (i.e., the higher the temperature, the lower the permissible working pressure, as shown in Figure 4.29). Furthermore, the physical properties change with time.
3. Careful handling is required in loading, unloading and installation.
4. Plastic pipe should be buried to protect it from sunlight (which will cause deterioration with time), mechanical damage, freezing and fire.
5. Weeping can occur in reinforced epoxy pipe.
6. Non-metallic pipe has very low resistance to vibration and pressure surging. Both reinforced epoxy and PVC piping is commonly downrated 30-50% from the manufacturer's recommended maximum working pressure to allow for pressure surging.

DISSOLVED GAS REMOVAL

Dissolved gas removal is covered in Chapter 6.

DESIGN TO MINIMIZE CORROSION

Many installations are designed in such a way that future failures are inevitable. Following are some recommendations which should be considered during the design of any injection or disposal project.

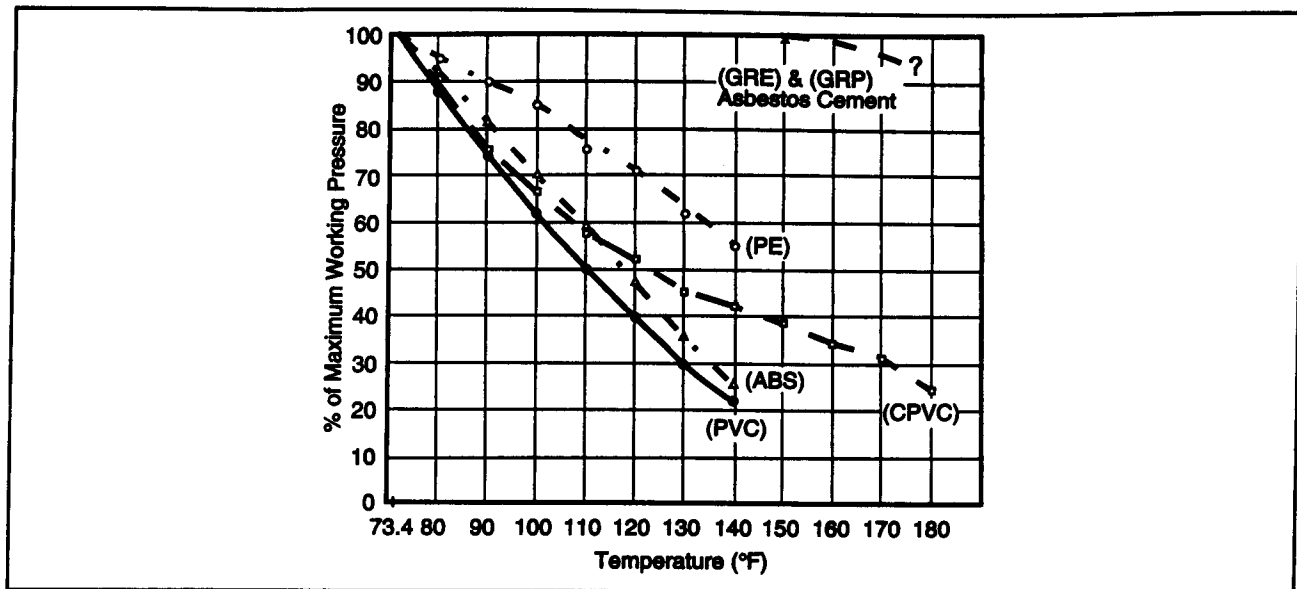


Figure 4.29 Temperature Limitations for Non-Metallic Piping^(4.56)

Avoid Crevices

Crevice corrosion has already been discussed and we know that crevices are bad. Some examples of man-made crevices are shown in Figure 4.30^(4.17)

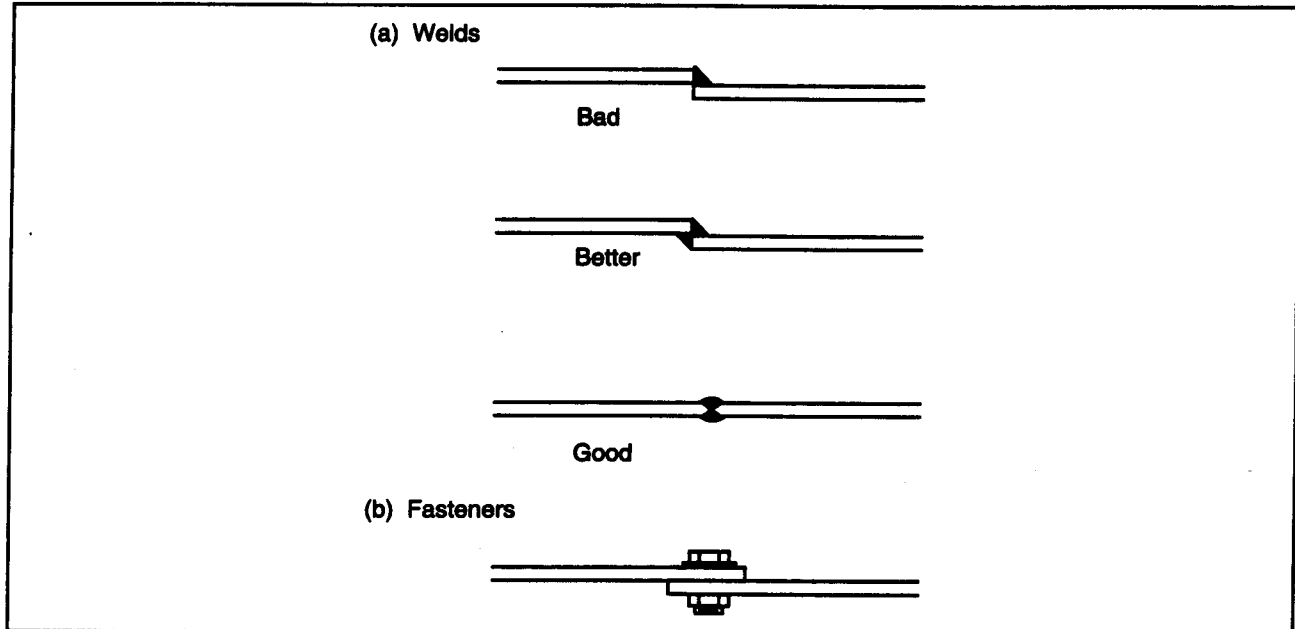


Figure 4.30 Welds and Fasteners

Avoid Low-Flow Areas

Solids or sludge will drop out and encourage the formation of concentration cells as well as creating ideal spots for bacteria to grow. The minimum velocity in pipelines should be 3 ft/s (1 m/s).

Avoid High-Flow Areas

Turbulent flow, especially when suspended solids or gas bubbles are present, leads to accelerated corrosion rates. Impingement or erosion corrosion can also result.

A long radius bend is sometimes used in place of an ell (the bend radius should be at least 5 times the pipe diameter), and the substitution of two 45° bends for a single 90° bend is quite effective in reducing problems inherent with sudden changes in fluid direction. Another popular and effective method is the substitution of a "blind" tee for an ell as shown in Figure 4.31.

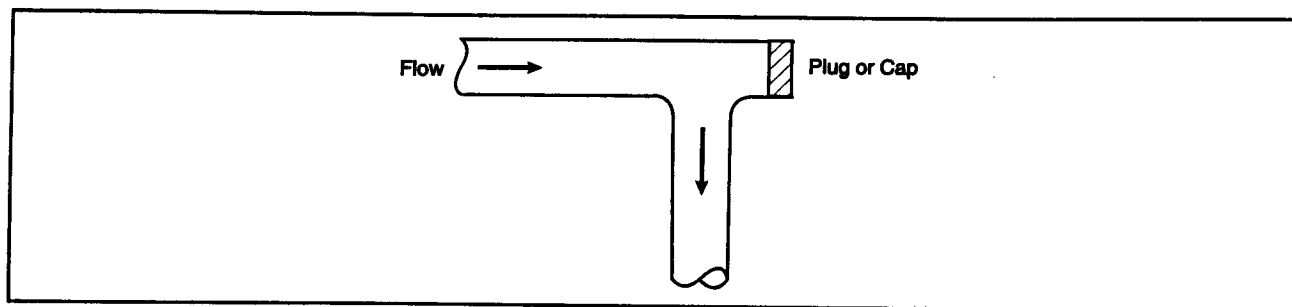


Figure 4.31 Blind Tee

Where economically feasible, it is recommended that fluid velocities be maintained in the range of 3-7 ft/sec [0.9-2.1 m/s].

Adequate Net Positive Suction Head

Pumps must be supplied with water at a pressure sufficient to prevent cavitation. It will also help prevent oxygen entry.

Materials Selection

Select linings, coatings or corrosion resistant materials to withstand the environment if that seems to be the most economical way to go. Use NACE Standard RP0475 as a guide.^(4.3) Do it at the outset, during the design stage. Avoid coupling dissimilar metals so that galvanic corrosion will not be a problem.

If hydrogen sulfide is present, or if there is reason to believe that it will be present at some future date due to bacterial activity, then the possibility of sulfide stress cracking must be considered.

The only completely effective method of preventing this form of failure is through selection of materials which will not crack. However, it should be noted that many materials which are immune to sulfide stress cracking, such as the low strength carbon steels, are still susceptible to weight loss corrosion. Normal corrosion control procedures are required to preserve the integrity of these types of materials.

NACE Standard MR0175 specifically states that materials selection for water handling facilities is "covered by other API and NACE Standards and is outside the scope of this Standard." However, the prudent operator would be well advised to select materials in conformance with this Standard for any portion of a system which falls in the sulfide stress cracking region as defined in Figure 4.32.

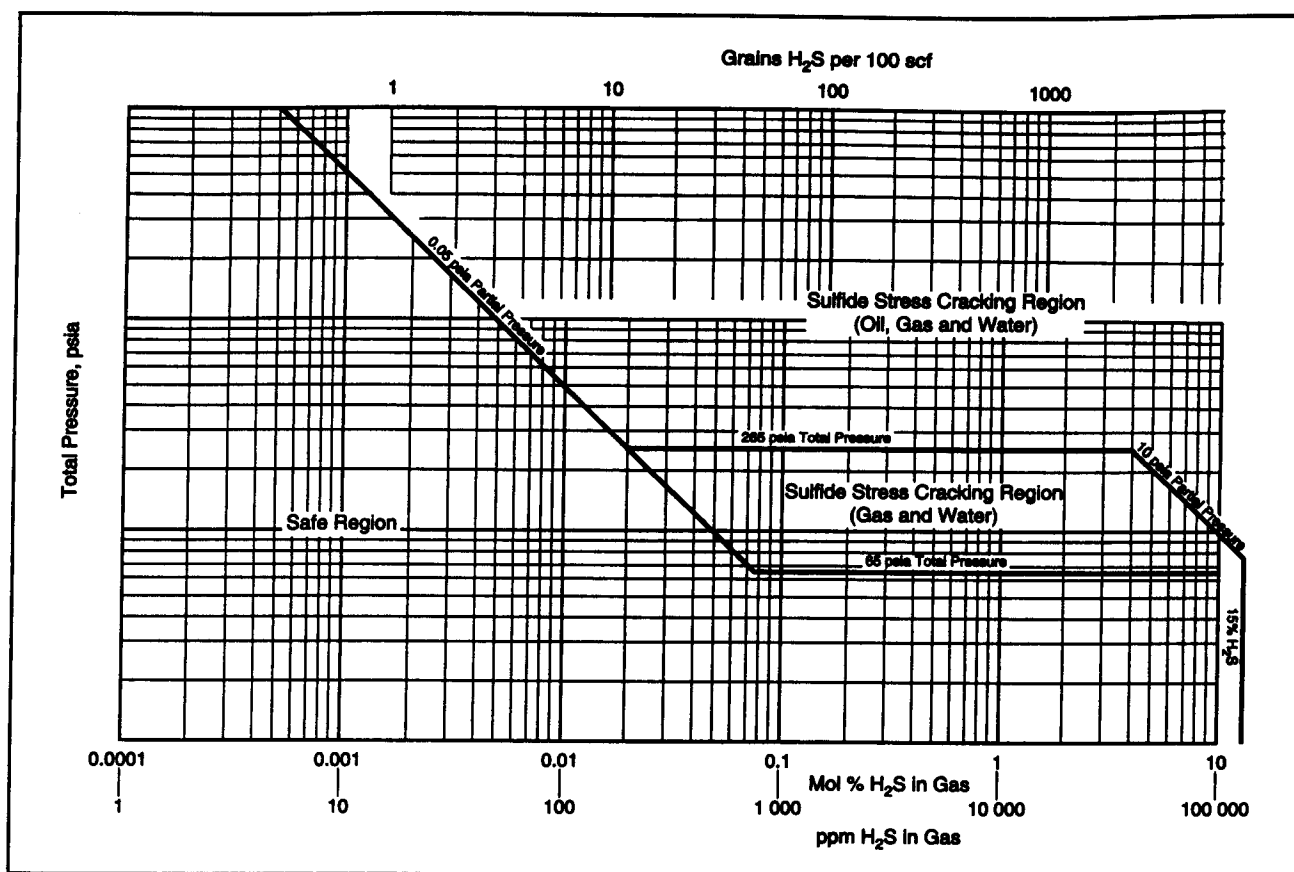


Figure 4.32 Sulfide Stress Cracking Regions

This diagram is divided into three regions:

1. The "safe region" for all fluids. No sulfide cracking problems would be anticipated, regardless of the fluids being handled or the materials employed.
2. Sulfide stress cracking problems would be anticipated for systems handling sour gas and water. Although intended for sour gas systems, it would also be applicable to sour water systems.
3. Sulfide stress cracking problems would be anticipated for multiphase systems handling sour crude oil, gas and water.

There are three situations where sulfide stress cracking problems might be encountered in water injection:

1. Naturally sour water is produced and reinjected.
2. A naturally sweet injection system becomes sour due to sulfate reducing bacteria activity.
3. A sweet oil reservoir becomes sour due to bacterial activity, resulting in sour produced fluids following breakthrough of injection water. This has occurred in several fields being flooded with seawater in the North Sea and in California.

If the produced fluids are disposed of and are not reinjected, as they typically are in offshore seawater floods, then potential cracking problems are confined to the production facilities. However, if they are reinjected, then the injection system must also be considered.

Many water injection systems will not be subject to sulfide stress cracking problems due to low pressures and/or low levels of hydrogen sulfide. However, there are an increasing number of high

pressure injection systems, and the possibility of reservoir souring by bacterial activity makes the possibility of sulfide stress cracking a very real concern in both the injection and production systems.

Common Sense

In short, a knowledge of the things which cause problems can save many dollars if applied during the design of a system. There is no substitute for common sense.

CORROSION MONITORING TECHNIQUES

Coupons

Coupons are simply pieces of metal which are inserted into a system to evaluate one or more of the following:

1. System corrosivity
2. Material performance
3. Inhibitor performance

They are weighed before being inserted into the system and after removal from the system to determine the amount of metal lost.

Types

A coupon may have several geometric shapes:

Flat Plates

These are commonly used in many systems. They are often mounted in pairs so that duplicate measurements can be made.

Rods

Metal rods, 0.25 inches [6.4 mm] in diameter, are in common use.

Discs

Disc-shaped coupons are mounted flush with the pipe wall. They are mounted on the bottom of the line, and are generally used in conjunction with the high pressure access systems discussed in the next section.

Spools

Short sections of pipe are mounted in the system in such a way that they can be removed for evaluation. They are commonly threaded or flanged on both ends.

Holdings and Insulators

Coupon holders are designed so that the coupon is isolated from the structure. If the coupon and the structure are electrically connected, the corrosion coupon will normally corrode faster than the structure of interest.

Holders should either be mounted in such a way that they can be isolated from the flow stream by valving for removal, or a special retractable holder may be used which can be withdrawn while the system is under full operating pressure.

Coupon Retrieval Systems

Two types of systems are available for the insertion and removal of coupons without system shutdown or depressurization as listed in Table 4.8.

TABLE 4.8
Coupon Retrieval Systems

Description	Maximum Working Pressure
Inserted and retrieved through stuffing box and packing gland with screw jack.	1500 psi [10,300 kPa]
Pressure-balanced retriever	6000 psi [41,400 kPa]

Low-pressure systems are made and marketed by several suppliers. Each system consists of a full opening valve (usually a ball valve) permanently mounted on the system, a stuffing box, a packing gland, and a lock nut to hold the mandrel in place against pressure.

The Rohrback Cosasco system is shown in Figure 4.33.

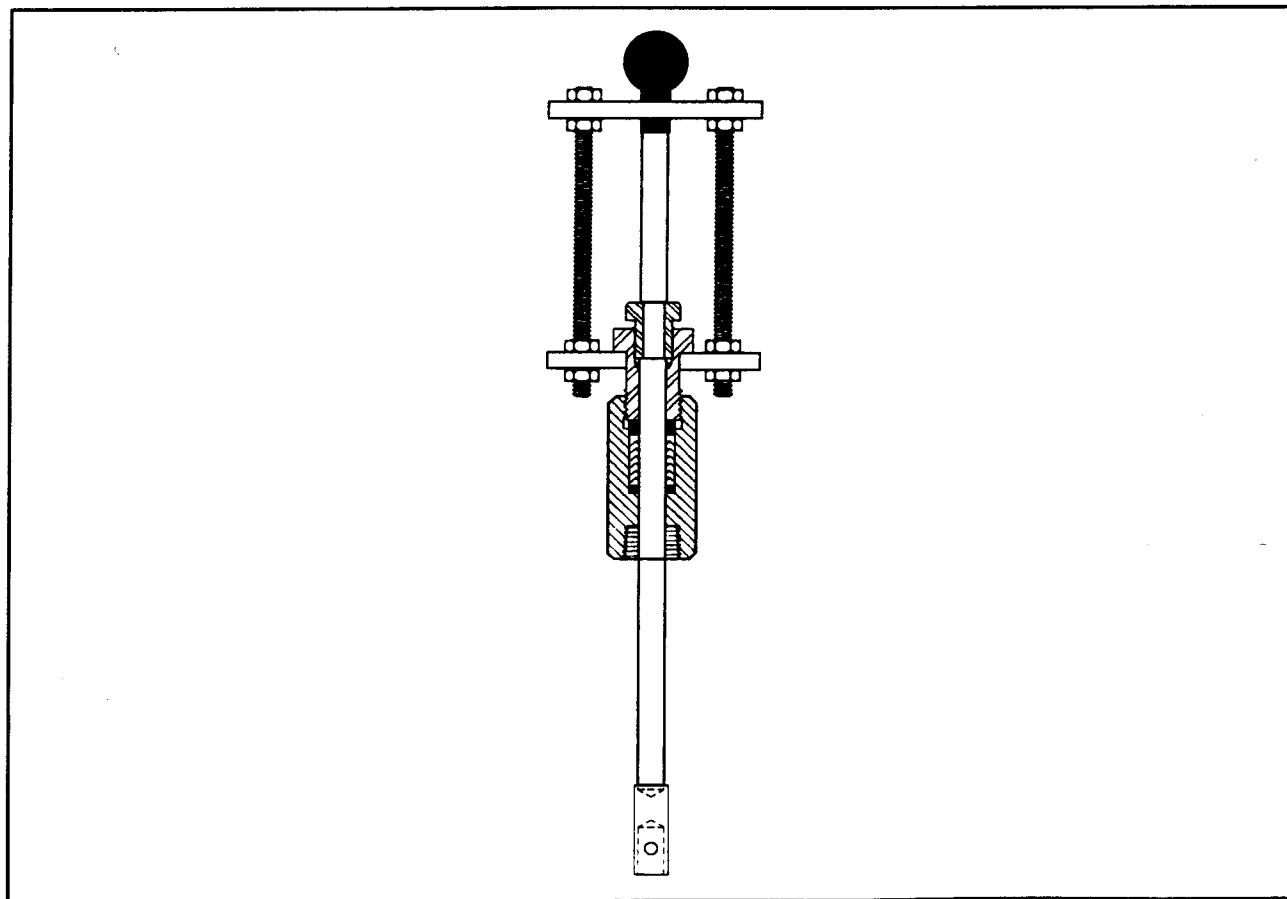


Figure 4.33 Low Pressure Coupon Retrieval System (Courtesy Cortest)

The high pressure systems consist of a permanently mounted access fitting, a removable carrier plug holding the coupon, and the pressure balanced retrieval system. Retrieval or installation is accomplished as shown in Figure 4.34.

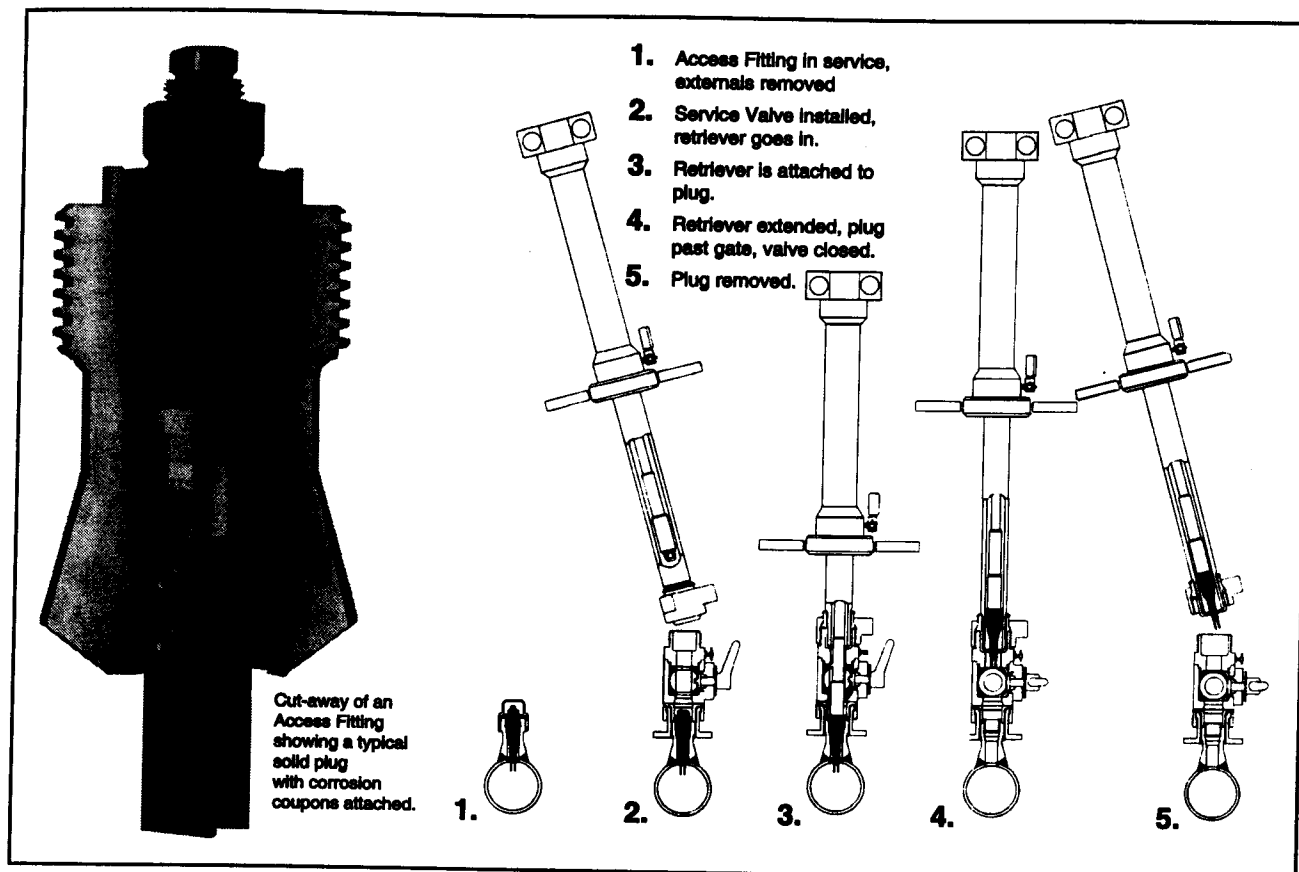


Figure 4.34 Rohrback Cosasco High Pressure Retrieval System

The unique feature of these systems is the ability to equalize or "balance" the pressure inside the retrieval tool with the system pressure. The pressure is the same on both sides of the carrier plug, so the system pressure exerts no force on the plug during retrieval or installation.

Coupon Handling

Try not to touch the coupon with your bare fingers when mounting it in a holder. Contact with a finger may result in increased or decreased corrosion at the point of contact in the shape of a finger print. Whether the corrosion is increased or decreased depends on whether your finger is salty or oily. Disposable plastic gloves are very handy for preventing this problem.

Coupon Location and Orientation

The coupon must be placed in a *representative* location, and oriented in such a way that it will not induce turbulence in the flow stream.

If a pitting attack is taking place along the bottom of the pipe, you may not detect it with a coupon located in the center of the stream. A pipe spool or a flush mounted disc coupon would be a better choice.

Coupon Evaluation

Coupons are supplied which have been sandblasted or surface ground and pre-weighed. When you remove them from the system, they should be examined for any pits or scale formation before sending them off to a laboratory for evaluation. You may want to request an analysis of the scale.

Calculation and Interpretation of Coupon Results

The coupons are cleaned of scale in the laboratory, and re-weighed. The amount of weight loss is treated as though it were uniformly removed from the total surface area of the coupon and converted into an average penetration rate. Corrosion rates are commonly expressed in mils of thickness lost per year (mpy) or millimeters of thickness lost per year (mm/y).

$$\text{Corrosion Rate} = \frac{\text{Weight Loss}}{\text{Exposure Time} \times \text{Coupon Surface Area} \times \text{Metal Density}}$$

$$\text{mpy} = 365000 \frac{W}{ADT}$$

Where:

- mpy = mils per year
- W = Weight loss, g
- A = Coupon surface area, in²
- D = Metal density, g/in³
- T = Exposure time, days

For steel, which has a density of 128.8 g/in³, the formula reduces to:

$$\text{mpy} = 2834 \frac{W}{AT}$$

The calculated corrosion rate should be rounded off to the nearest tenth of an mpy.

In SI units, the formula for steel is:

$$\text{mm/y} = 465 \frac{W}{AT}$$

Where:

- mm/y = millimeters per year
- W = Weight loss, g
- A = Coupon surface area, cm²
- T = Exposure time, days

This corrosion rate is significant in systems where uniform corrosion occurs. However, it is relatively meaningless in pitting systems, because all of the weight loss is occurring in a few isolated spots on the coupon. The number, depth, and diameter of the pits should be noted.

Coupon exposure times vary depending on the corrosivity of the system. Corrosion rates usually start out high on the fresh metal surface of the coupon and very short exposures may give unrealistically high rates. Exposure periods of 30-90 days are common.

Often, pitting corrosion will not occur on a coupon even though corrosion is occurring in the system. Although this can be due to many factors, one common cause is that the coupon exposure period is too short. Exposure periods of 6 months or more are often necessary to detect pitting on a coupon. This is due to the fact that pitting often doesn't begin immediately after a piece of metal is

placed in water. There is usually a delay before pitting begins. However, once a pit is initiated, it usually deepens very quickly.

This means that it may be desirable to maintain two sets of coupons in a system: one set exposed for 30-90 day periods to measure changes in general corrosion rates, and a second set exposed for periods of 180 days or more to monitor pitting corrosion rates.

Very low corrosion rates are drastically influenced by cleaning loss. Cleaning loss is the amount of metal which is removed from the coupon during the cleaning operation. Depending on the cleaning method, this can easily amount to 0.5 mpy. Cleaning loss is not subtracted by most commercial laboratories when they report results. Thus, if a corrosion rate of 1.0 mpy is reported, the actual weight loss due to corrosion may be only $1.0 - 0.5 = 0.5$ mpy.

Of course, you are usually interested in changes in corrosion rate rather than the absolute value, and cleaning loss should remain reasonably constant, so it is not normally critical.

Evaluation of Pipe Spools

Spools are usually too heavy to weigh, and are split open for visual evaluation and calipered to determine any reduction in wall thickness.

The following evaluation procedure is recommended:

1. Mark the top of the spool and the direction of flow.
2. Remove the spool from the system and replace it with a new spool.
3. Split the spool longitudinally in the horizontal plane with a saw or welding torch.
4. Photograph the internal surfaces of the top and bottom sections.
5. Remove samples of any scale or deposited solids from both the top and bottom segments and send them to a laboratory for analysis.
6. Clean the internal surfaces thoroughly with a wire brush and photograph again.
7. Note the general condition of both halves of the spool.
8. Count the number of pits and measure their depths. Calculate the pitting rates based on the exposure period.

The primary advantage of a spool over a coupon is that it is an actual piece of the system. The true condition of the pipe surface can be determined. The type of attack and its location on the circumference of the pipe can be ascertained. This can be very important, as corrosion is often confined to a specific segment such as the bottom 90° quadrant.

Use of Coupons to Monitor Inhibitor Performance

When monitoring the performance of an inhibitor it is advisable to first determine the uninhibited corrosion rate in the system as a base. Once this has been established, corrosion inhibition is initiated and coupons are mounted in the system. Inhibitor performance is usually measured in terms of Percent Protection.

$$\% \text{Protection} = \frac{\text{Uninhibited Rate} - \text{Inhibited Rate}}{\text{Uninhibited Rate}} \times 100$$

Linear Polarization Meters — Instantaneous Corrosion Rates

Coupons give a direct measurement of metal lost over some period of time. Linear polarization measurements give a reading of the corrosion rate occurring on a coupon or “electrode” at the moment the measurement is being made.

Theory

A source of current is connected between two metal electrodes and a small amount of current is made to flow between the two electrodes. An electrolyte, such as water, must be present to conduct current between the probes. This current flow changes the potential of the “test” electrode. It has been shown that the corrosion rate (or more precisely the corrosion current) is proportional to the test current divided by the change in potential when the potential change is small (20 mv or less). So we apply sufficient current to the test electrode to change its potential by a specific amount (say 10 mv), and measure the amount of current required to effect the change.

$$\text{Corrosion Rate} = K \frac{\Delta I}{\Delta E}$$

Where: ΔI = Current necessary to change potential of test electrode by 10 mv
 ΔE = 10 mv
 K = Calibration factor which is a function of the size of the electrode and the type of metal

Types of Instruments Available

Linear polarization meters are available in either 2-electrode or 3-electrode models.

When a two-electrode probe is used in fresh water, the reading must be corrected for solution resistivity. No correction is required in most salt waters and the corrosion rate may be read directly from the instrument. The potential change of the test electrode is measured with reference to the second, or “working” electrode. (Figure 4.35)

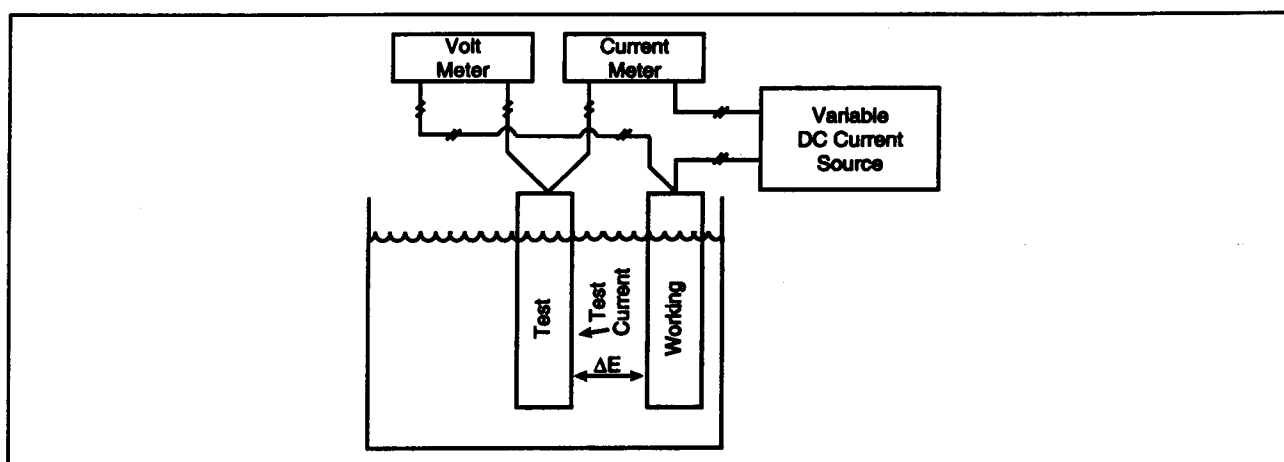


Figure 4.35 Schematic of Two-Electrode Linear Polarization Meter

A three-electrode probe requires no correction for solution resistivity and a direct readout of corrosion rate in mpy is possible. In the three-electrode model, the third electrode is allowed to corrode freely (no current is applied to it), and it is used as the reference electrode. (Figure 4.36).

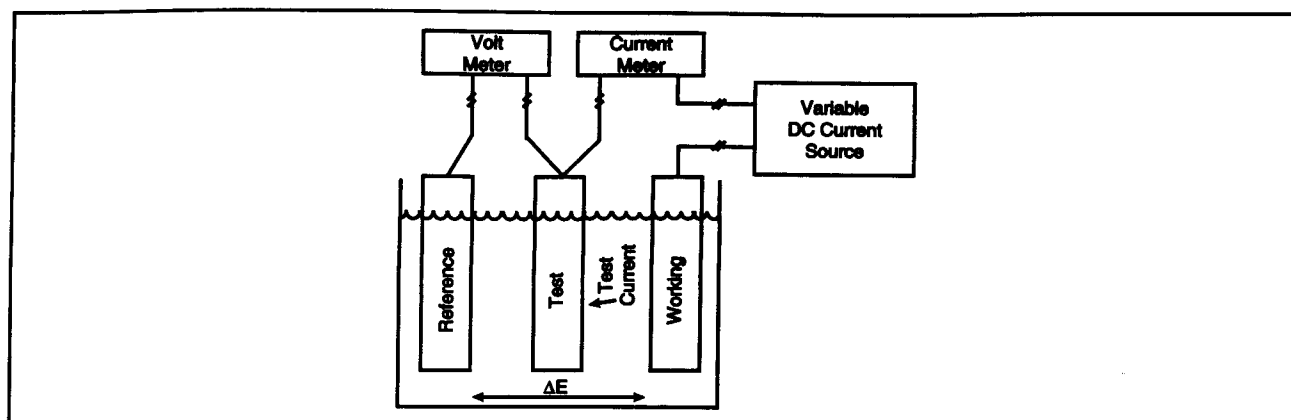


Figure 4.36 Schematic of Three-Electrode Linear Polarization Meter

Both two and three electrode probes are available with replaceable probe elements which may be utilized as weight loss coupons. Probes are also available in the form of flush mounted probes designed primarily for use in pipelines. Either single-reading meters or recording meters are available. The recording meters are available in either single-channel or multi-channel models.

Taking Readings

Single readings can be taken with a small battery-powered meter which can be carried around to various probe locations. In many cases this is adequate. In other cases, a recording meter should be left hooked up to the electrode for an extended time period. In all cases, probes should be mounted in the system and left there long enough to “age” or become accustomed to the environment so that representative corrosion rates may be measured.

The use of recording meters has proven to be extremely valuable, especially in systems where the corrosivity seems to change without reason. Many systems are corrosive only on a part-time basis. When certain conditions are present the system may suck in air, for example. A spasmodic problem is very difficult to solve without a continuous record of corrosion rate, which can then be correlated with other events to find the cause of the problem.

Pitting

One of the problems with linear-polarization readings is that they do not measure pitting rates. The tendency to pit can sometimes be inferred by changes in the natural potential difference between two electrodes without any applied current. This approach is not very reliable.

Probe Removal

Probes should always be mounted in such a way that they can be removed from the system, either by providing isolation valving or by using retractable probes. Some typical installations are shown in Figure 4.37. Probes should be removed periodically, cleaned, and inspected visually for signs of pitting.

Probes sometimes short out due to accumulation of iron sulfide between the electrodes. This requires removal for cleaning.

The probe elements, or in some cases the probe assembly, must be replaced periodically, which necessitates removal. If they are pre-weighed prior to installation, they can also be used as corrosion coupons.

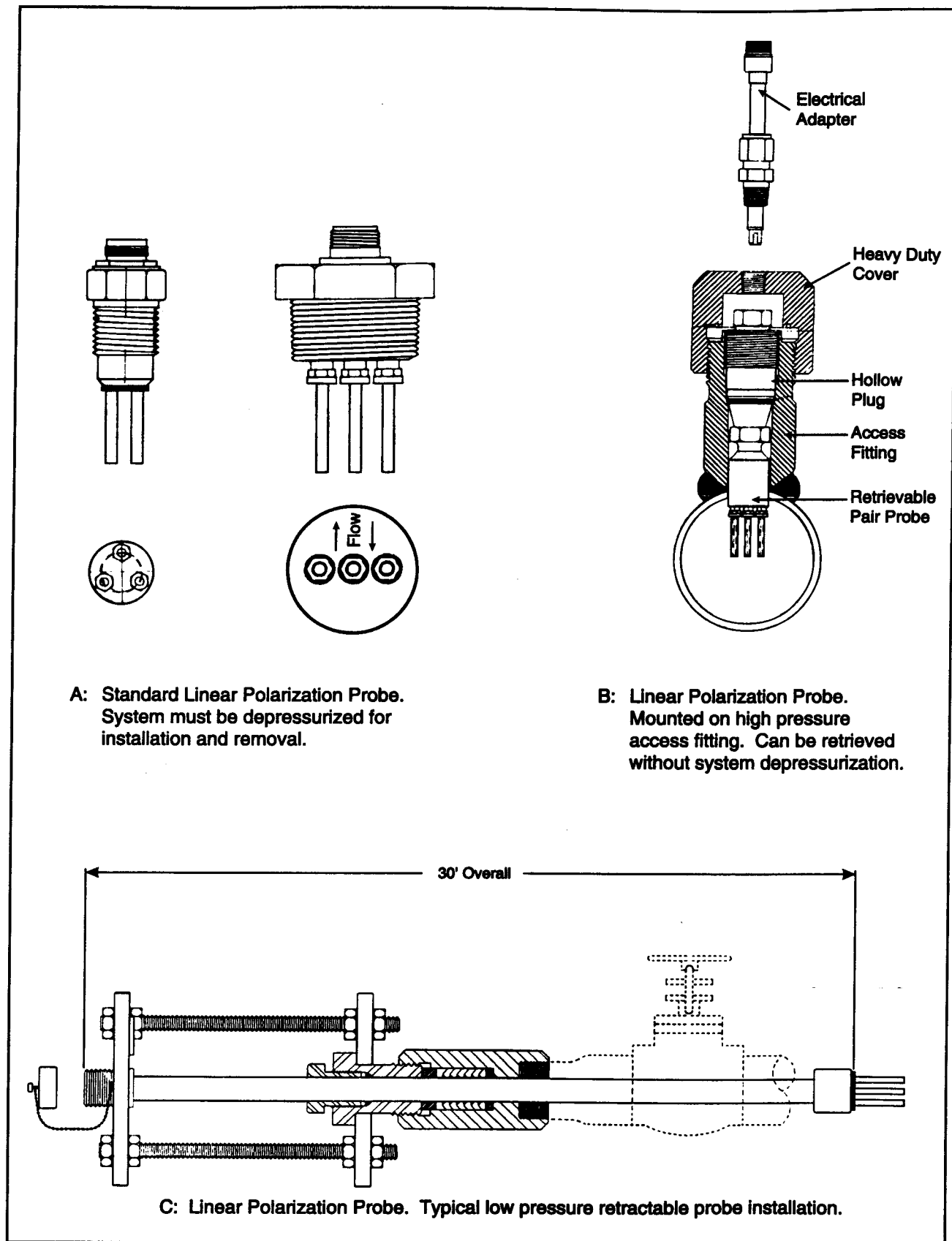


Figure 4.37 Linear Polarization Probes and Probe Installations (Courtesy Cortest)

Potentiodynamic Polarization Studies

Potentiodynamic polarization studies performed in the field provide a rapid means of estimating the pitting corrosion rate. It is the only method available capable of this feat, and is an invaluable tool to evaluate the effectiveness of inhibitors to control pitting. It is normally used on a periodic basis rather than as a continuous monitor.

General corrosion rates can also be estimated by this method. However, these rates can be measured more easily by linear polarization.

A potentiodynamic instrument is an electronic device that can control the electrochemical potential of a small piece of metal immersed in water (an "electrode") by the application of DC current.

When the electrode potential is changed over a range of values, the electrode is said to have been "polarized." A plot of the logarithm of current density (amount of applied current/electrode surface area) versus the electrode potential is called a polarization curve. A curve generated by a continuous change of the potential at a constant rate is called a potentiodynamic polarization curve.

In order to study corrosion phenomena it is usually necessary to run two separate polarization curves, or "scans." The cathodic curve is generated by applying current *to* the electrode, resulting in successively more negative potentials. The anodic curve is the result of drawing current *from* the electrode, giving increasingly positive potential values.

The technique as described by Martin^(4.58) is summarized as follows:

1. Insert a three-electrode probe into the system and allow it to come to equilibrium with the system. One electrode is used for the cathodic curve, one for the anodic curve, and the third is used as a reference electrode.
2. Perform a cathodic potentiodynamic scan.
3. Execute an anodic scan on a different electrode, this time reversing the scan direction at a current density of about 5 mA/cm². If this back anodic scan shows positive hysteresis, its intersection with the cathodic curve gives a current density proportional to pit growth in the system at the time of the test.
4. Remove the anodic test electrode from the system and determine the ratio of the unpitted area to the pitted area. (A typical value in many systems is 20/1.)
5. Calculate the pitting rate using the following equation:

$$\text{Pitting Rate (mpy)} = 455 \times \text{PCD} \times \text{PAR}$$

Where: PCD = Pit current density, mA/cm². The intersection of the anodic back scan with the cathodic curve.
 PAR = Pitted area ratio. The ratio of the unpitted area to the pitted area.

An idealized plot of the polarization curves for carbon steel in an oilfield brine is shown in Figure 4.38. Calculation of the pitting rate is as follows:

$$\text{PCD} = 0.005 \text{ mA/cm}^2; \text{ PAR} = 20$$

$$\text{Pitting Rate} = (455)(20)(0.005) = 45.5 \text{ mpy}$$

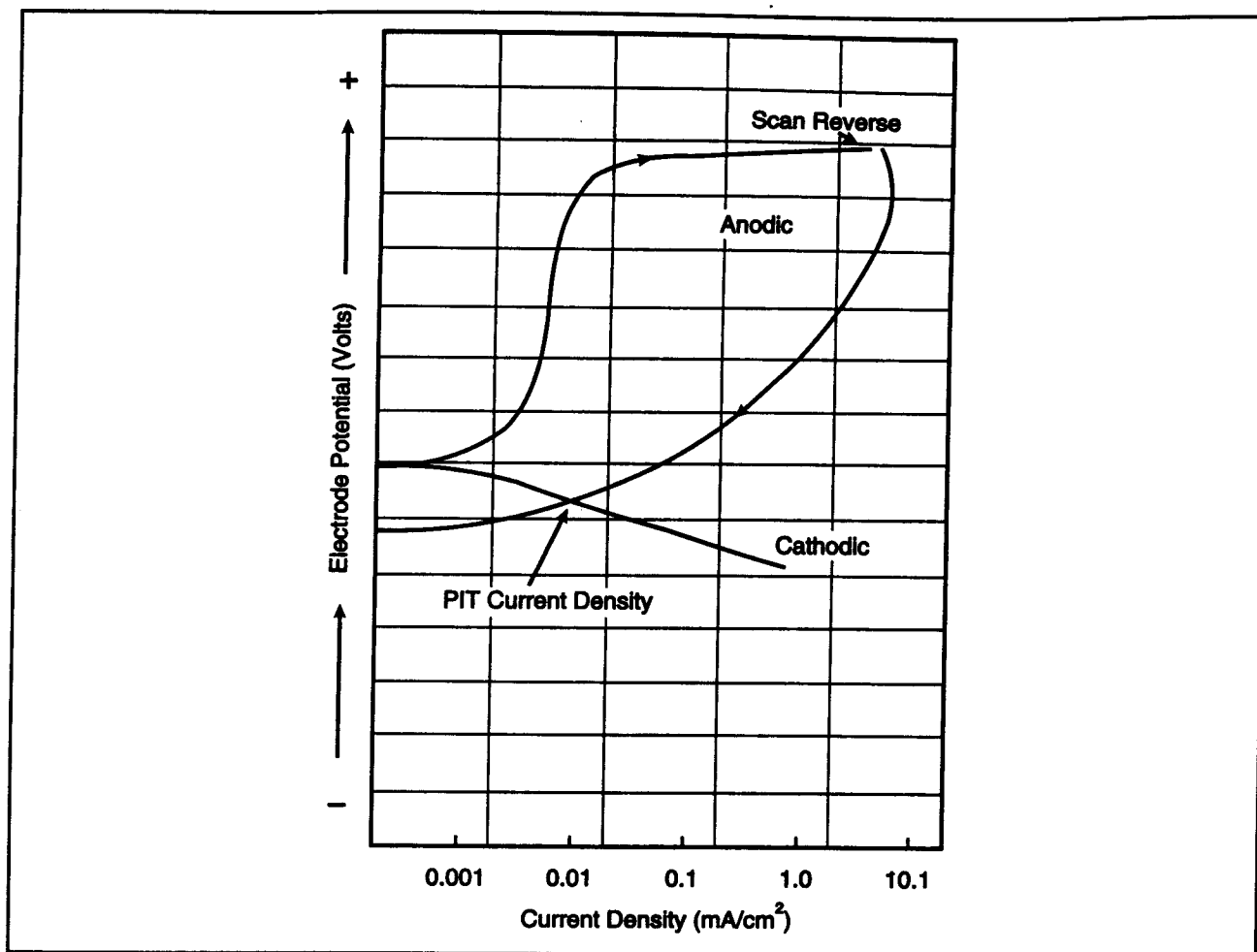


Figure 4.38 Typical Potentiodynamic Polarization Curve^(4.58)

Electrical Resistance Probes

The most widely used resistance probes utilize a loop of wire which is inserted into the system and allowed to corrode. The electrical resistance of the wire is inversely proportional to its cross-sectional area.

$$R = \rho \frac{L}{A}$$

Where:

R = Resistance of wire

ρ = Resistivity of the wire material

L = Length of wire

A = Cross-sectional area of the wire

Therefore, as the wire corrodes away, its cross-sectional area is reduced and the resistance increases.

An instrument is attached to the probe which measures the ratio of the resistance of the wire that is exposed to corrosion to the resistance of an internal reference wire that is protected from corrosion. (Figure 4.39) The resistance of the exposed wire is affected by temperature as well as wire diameter.

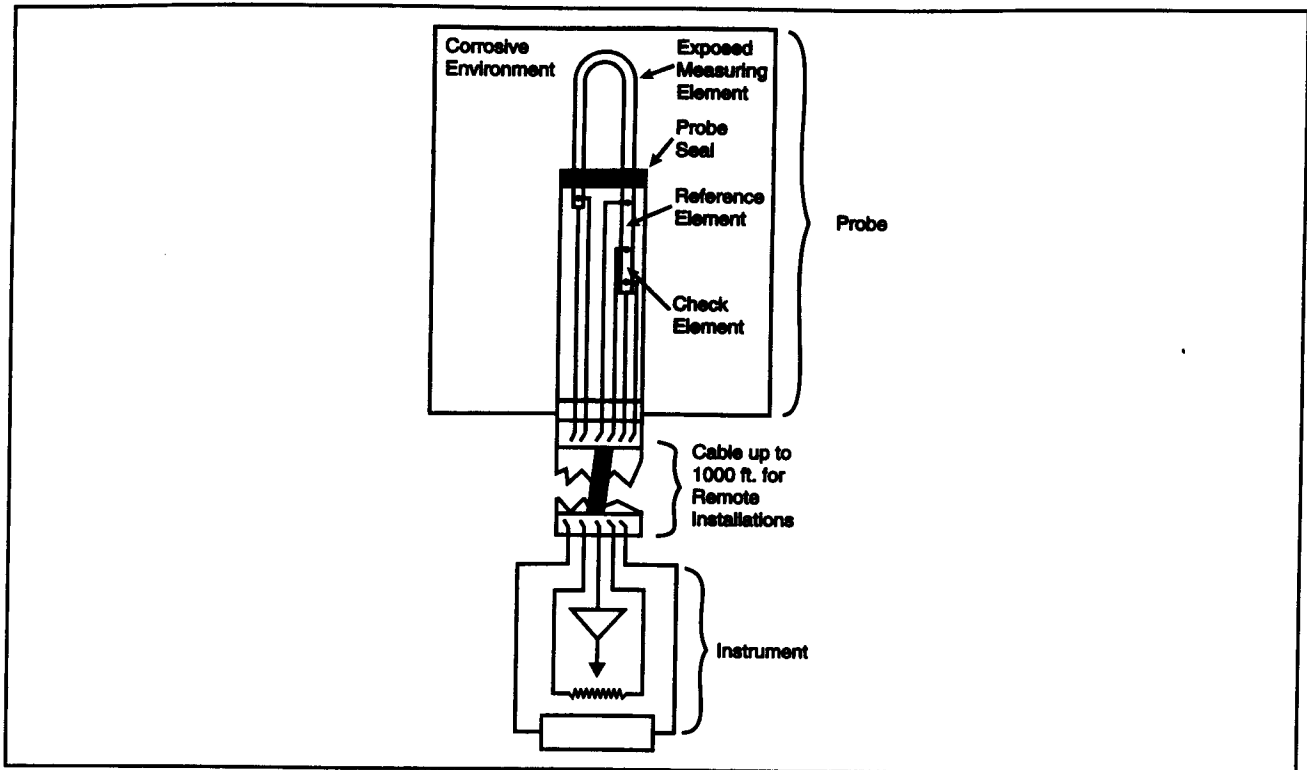


Figure 4.39 Schematic of Corrosometer Electrical Resistance Probe (Courtesy Rohrbach Cosasco)

By measuring the ratio of the two resistances, temperature changes that equally affect both wires are canceled out and the readings are directly proportional to the diameter of the exposed wire.

The instrument readings are plotted versus time, and the slope of any straight line portion of the curve may be converted to a corrosion rate, as shown in Figure 4.40. It does not provide instantaneous data like linear polarization measurements.

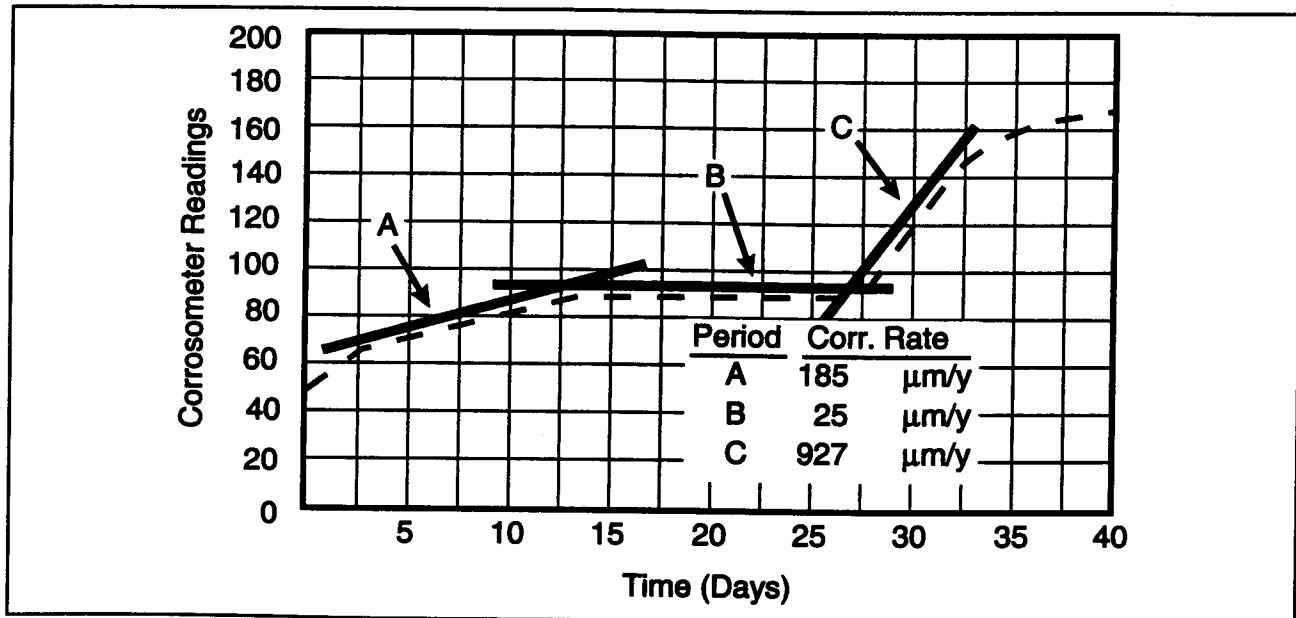


Figure 4.40 Typical Corrosometer Data (Courtesy Rohrbach Cosasco)

Probe elements other than wires are also available as illustrated in Figure 4.41. Small, strip-type elements can be mounted flush to a pipe wall. Thin-walled, tube-type elements are used when high sensitivity is required for measurement of low corrosion rates.

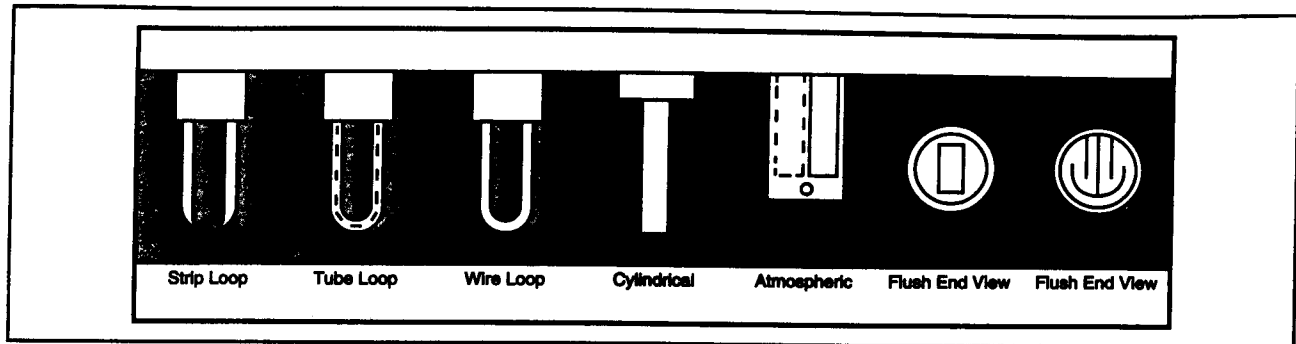


Figure 4.41 Corrosometer Probe Element Styles (Courtesy Rohrback Cosasco)

Resistance probes do not require a conductive electrolyte and are often used in gas systems as well as in aqueous systems.

Detection of pitting is also a problem with resistance probes. Visual inspection is still the only reliable way to determine the type of attack.

Accumulation of conductive corrosion product (like iron sulfide) on the probe wire can cause a decrease in resistance, resulting in an apparent decrease in corrosion rate. Shorting can also occur. Once again, the probes should be removed periodically, cleaned and examined.

Galvanic Probes

When two dissimilar metals are immersed in water and connected together with a wire, current will flow between them because of their natural potential difference. The amount of current flow is a direct function of the corrosivity of the system.

Commercial probes typically utilize a brass probe and a steel probe connected to a microammeter to measure the current flow as shown in Figure 4.42.

Recording microammeters are most commonly used with this type of probe. It is quite inexpensive compared to other monitoring instruments. However, it does not give a readout in mpy, and its primary utility is in detecting changes in the corrosivity of the system. Therefore, the use of a recording model is highly recommended. Anything which will cause a change, such as velocity, pH or dissolved oxygen, will cause a change in current. However, they are extremely responsive to the presence of dissolved oxygen and are most commonly used as "oxygen detectors."

Figure 4.43 compares the response of a galvanic probe and an oxygen meter to very small quantities of dissolved oxygen in a specific water. The scale for the oxygen meter is 0-0.84 mg/L and the galvanic probe scale is 0-400 A.^(4.59)

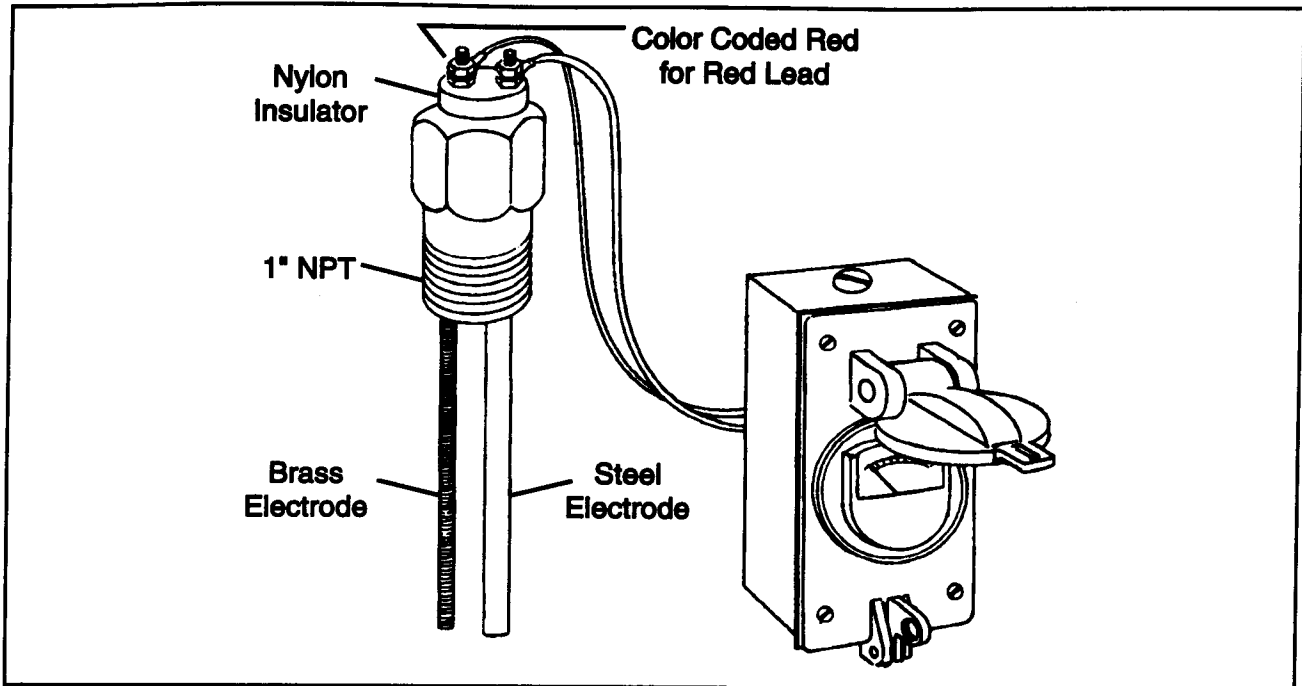


Figure 4.42 Galvanic Probe Assembly^(4.59)

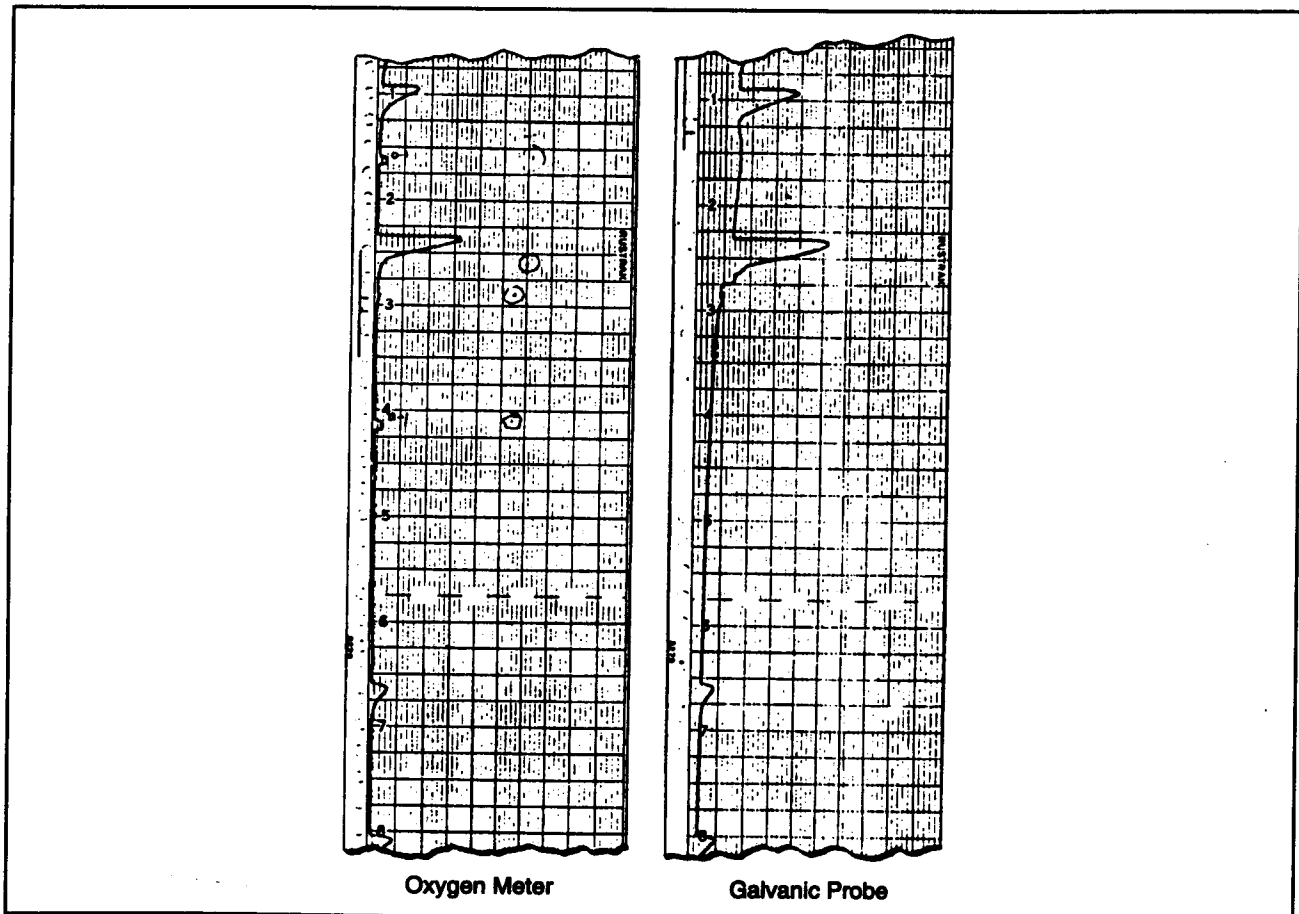


Figure 4.43 Comparison of Galvanic Probe and Oxygen Meter Response^(4.59)

Hydrogen Permeation Rate Measurement

As explained previously, many of the hydrogen atoms generated by corrosion in sour systems enter the steel. The rate at which atomic hydrogen permeates the pipe wall is an indirect indication of corrosion rate in sour systems.

Pressure Hydrogen Probe

The simplest device for the detection of hydrogen permeation is a hydrogen probe. It is a hollow, thin walled, steel tube which is sealed on one end and equipped with a pressure gage on the other end. The tube is inserted into the system and corrosion occurs on the external surface of the tube. Hydrogen generated by the corrosion reaction permeates through the wall of the tube into the hollow interior, causing the pressure to increase. The rate of pressure increase is proportional to the corrosion rate.^(4.60,4.61)

Electrochemical Hydrogen Probe

Another method of measuring hydrogen permeation rates utilizes an electrochemical cell which is attached to the outside surface of a pipe or vessel and referred to as a "patch probe". The hydrogen generated by corrosion on the internal surface of the equipment travels through the steel wall into the cell where the hydrogen is detected and "counted."^(4.60-4.62)

Two different types of hydrogen probes are illustrated in Figure 4.44.

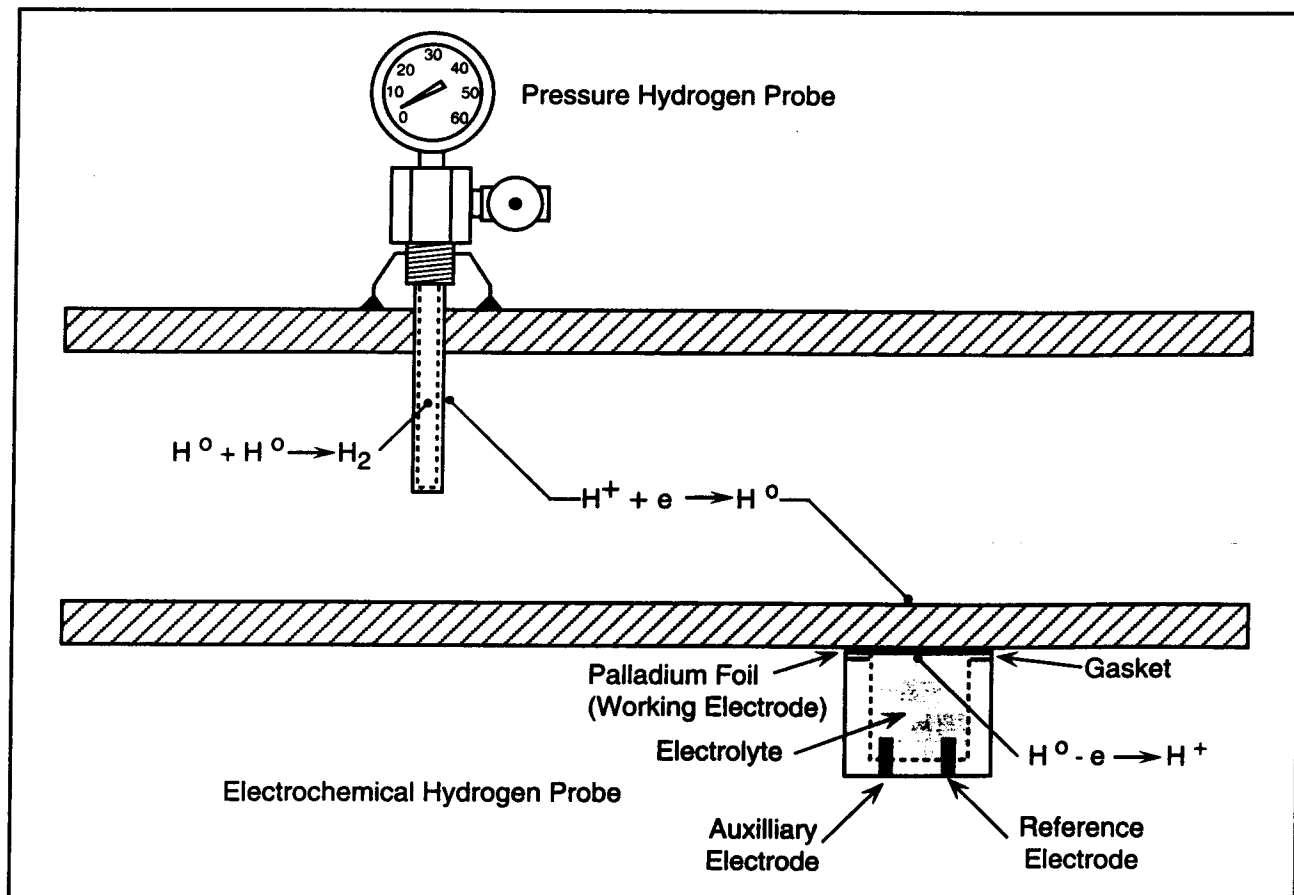


Figure 4.44 Hydrogen Probes

Dissolved Gas Analysis

Since we know that the presence of even very small amounts of dissolved oxygen can cause severe corrosion, measurement of dissolved oxygen concentrations using CHEMets (see Chapter 2) or an oxygen meter is extremely important in systems which are supposed to be air-free.

Dissolved H_2S concentrations are routinely measured in normally sweet systems as a means of detecting the presence of sulfate reducing bacteria.

Corrosion Product Analysis

Analysis of corrosion products can often be extremely valuable in determining the cause of corrosion. For example, the appearance of iron sulfide in a normally sweet system would indicate the probable presence of sulfate reducing bacteria.

Iron sulfide will oxidize when exposed to air and convert to iron oxide. Therefore, a laboratory analysis may show iron oxide when in reality the corrosion product was originally iron sulfide.

Iron Counts

Iron counts, or more precisely, the dissolved iron concentration in the water can be a good measure of the amount of corrosion occurring in a system. However, several precautions should be taken to assure good results.

1. **Natural Iron**

Determine if there is any "natural" iron in the water. Some formation waters naturally contain a few ppm iron even when no corrosion is occurring.

2. **Precipitated Iron**

Of primary concern is the amount of iron dissolved in the water in systems containing little or no oxygen. This means a single speck of solid corrosion product can give erroneously high readings. Also, exposure of the water to air will cause the dissolved iron to precipitate as ferric hydroxide. Therefore, it is desirable to filter the sample immediately after sampling to remove any precipitated iron.

Then even if the iron precipitates from the filtered sample, we know that it was dissolved at the time of sampling and the sample can be acidified to put the iron back in solution for analysis.

3. **Oxygenated and Sour Systems**

Iron counts in systems which are thoroughly aerated or which contain H_2S are of limited value. The primary problem is that the iron being dissolved by corrosion is usually precipitated somewhere in the system and very little stays dissolved in the water.

Inhibitor Concentrations

Inhibitor concentrations in a fluid can be determined in several ways. If you are interested in measuring inhibitor concentrations, contact the chemical company of your choice, and they will give you the details.

Bacteria Counts

Determination of the bacteria content of a water is another indirect method of inferring corrosivity. It is covered in Chapter 5.

Downhole Inspection

Mechanical-Multifinger Caliper Tools (Tubing and Casing)

Mechanical caliper tools are run in wells on wirelines to detect internal corrosion of tubing or casing. A continuous profile is measured by spring-loaded mechanical feelers arranged around the circumference of the tool which are forced against the inner pipe wall. A continuous log is produced which shows the profile of the internal surface of the tubing or casing in varying degrees of detail.

There are three types of tools available:

1. Maximum Recording

This tool produces a single trace which is a recording of the displacement of the feeler which has extended the furthest distance from the tool. It does not tell you how many feelers extended that distance. This means that a pit contacted by a single feeler would produce the same record as circumferential corrosion contacted by all feelers if both the pit and the circumferential corrosion were the same depth.

2. Minimum-Maximum Recording

There are two types of tools available which continuously record both minimum and maximum feeler extension. The simplest tool produces a two-line recording indicating minimum and maximum internal diameter measurements. There is also a tool which records 3 minimum and 3 maximum measurements, one each per 120° section, or 6 maximum caliper measurements, one per 60° section.

3. All-Feeler Recording

This tool continuously records the extension of all feelers. The record will consist of as many lines as there are feelers, making it possible to determine the pattern of attack as shown in Figure 4.45.

Electromagnetic Induction (Casing)

There are two types of casing inspection tools which utilize magnetic field induction to detect both internal and external casing corrosion.

DC Electromagnetic Induction

Typical downhole DC tools consist of one or more circular arrays of sensor pads, also called shoes, mounted so as to be in close proximity of the inside casing surface. The tool saturates a section of casing between the poles with an induced electromagnetic field, setting up symmetrical lines of magnetic flux as shown in Figure 4.46. If there is an anomaly in the pipe wall such as a pit or hole, the symmetry of the flux patterns is disturbed, and *flux leakage* occurs. The flux leakage is detected and measured by the sensor pads as they pass through the area of flux leakage. This measurement will detect both internal and external corrosion.

Simultaneously, a high frequency AC current is used to generate a magnetic field which will induce eddy currents in the interior wall of the casing. In most tools, the eddy currents penetrate only

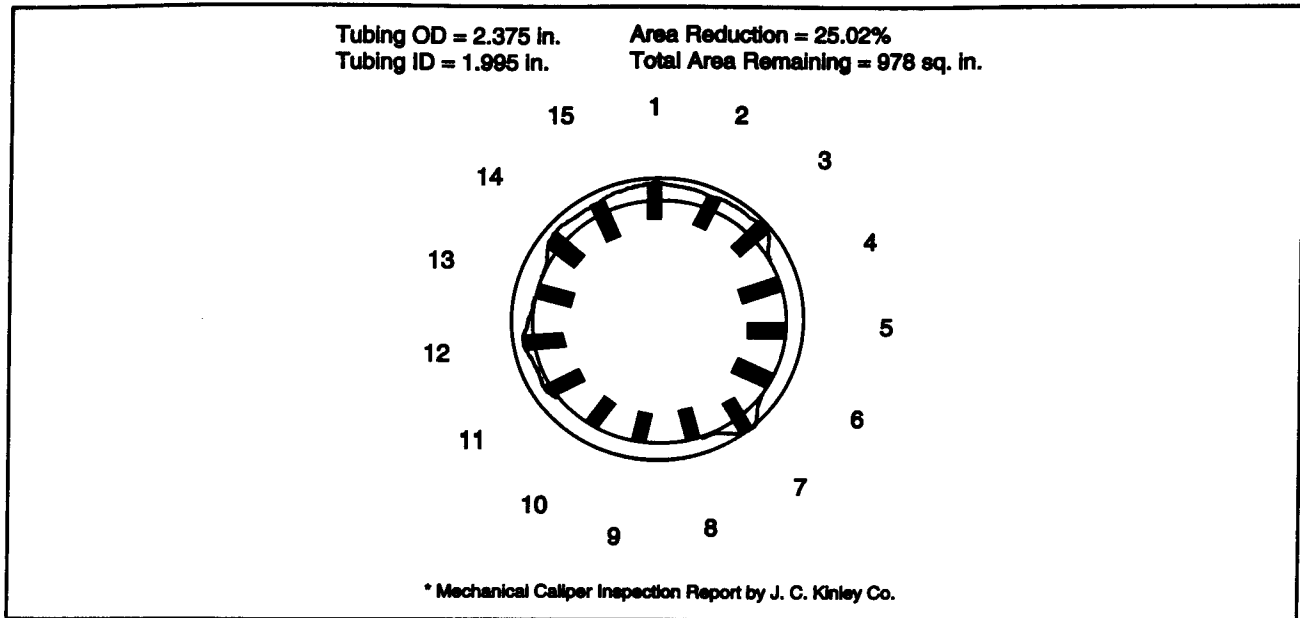


Figure 4.45 Cross Section of Corroded Production Tubing^(4.63)

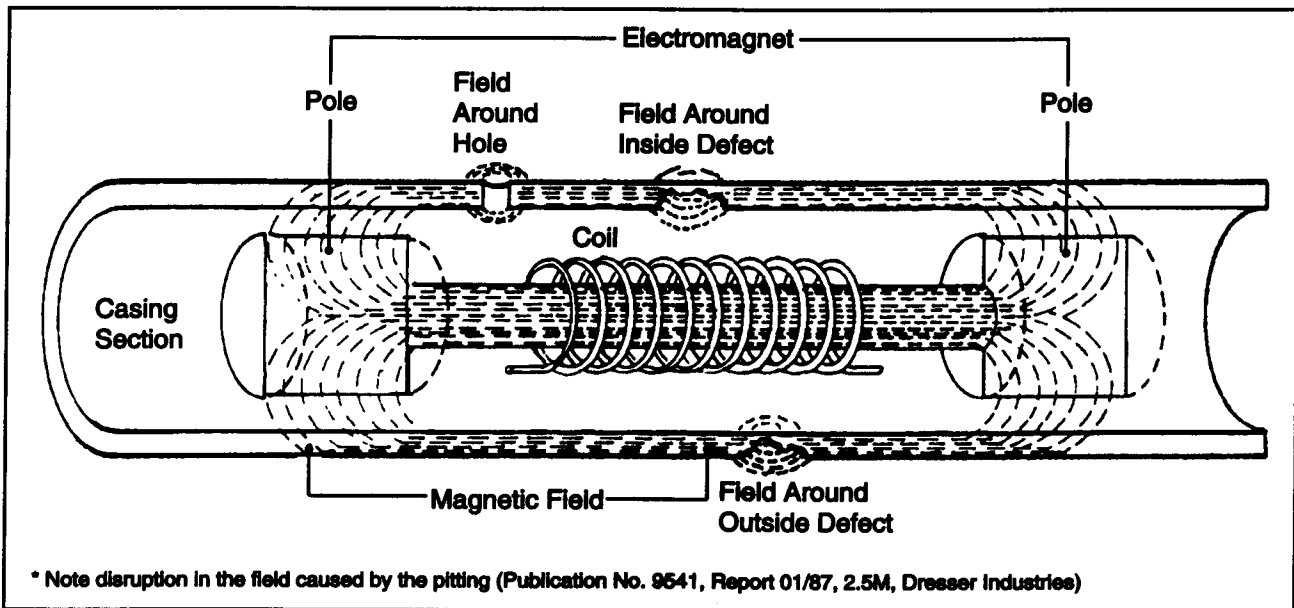


Figure 4.46 Downhole Electromagnetic Inspection Tool ^(4.63)

about 1 mm into the casing wall. An eddy current response is indicative of metal loss on the internal surface. Defects on the outer surface of the casing are not detected by eddy current testing due to the shallow depth of investigation.

Comparison of the flux leakage and eddy current responses make it possible to differentiate between internal and external corrosion damage as shown in Figure 4.47.

This type of instrument typically cannot detect pit depths which are less than 20% of the casing wall, or less than 0.25 inches (6.35 mm) in diameter. Pit-depth accuracy is approximately 15% of the pit depth under ideal conditions where all casing properties (weight, grade, etc.) are known. ^(4.65)

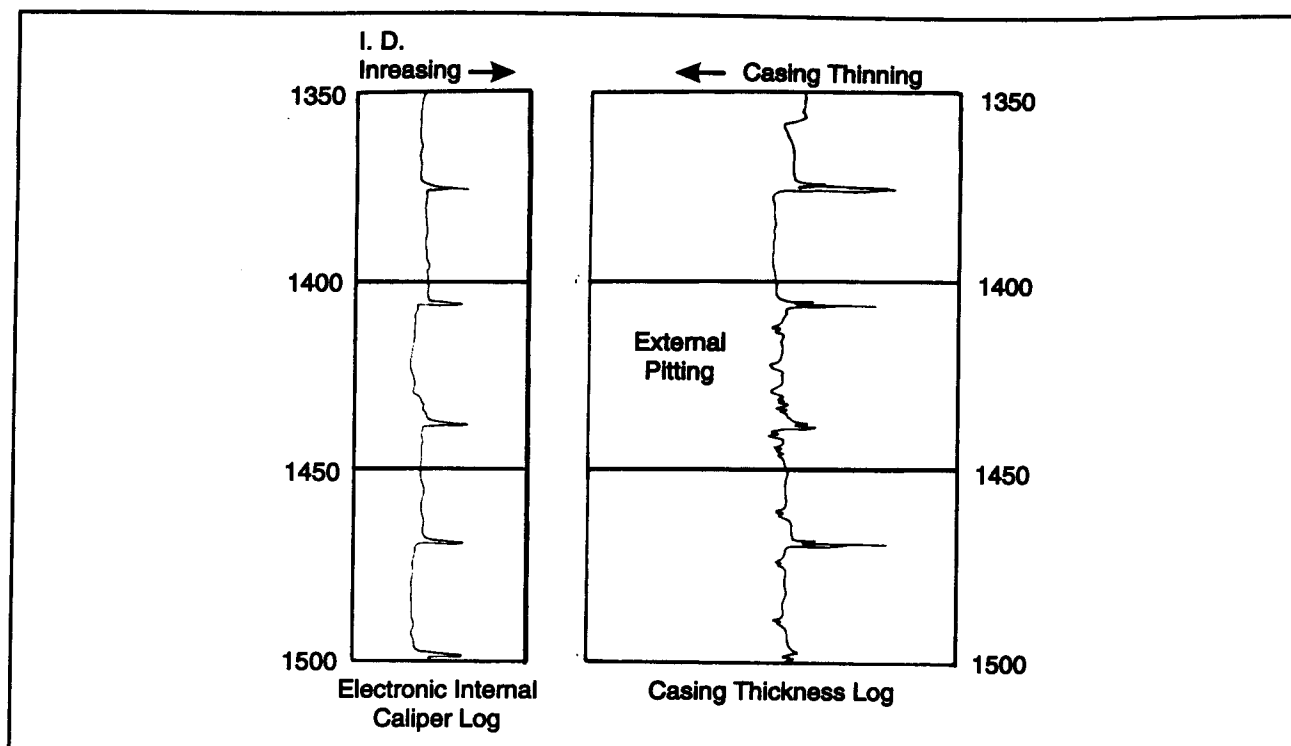


Figure 4.47 Typical Response of DC Electromagnetic/Eddy Current Inspection Tool^(4.64)

AC Electromagnetic Induction

There are two types of tools which fall in this category. In both cases a low frequency AC current is passed through a transmitter coil to induce an electromagnetic wave in the casing wall. The wave is detected by a receiver coil(s) located 12 to 24 inches (305-610 mm) away. The amount of phase shift or change of amplitude of the received signal(s) is used to calculate wall thickness. (Figure 4.48)

- Type 1

The measurements made by this type of tool do not account for changes in magnetic properties or casing grade, and are not considered suitable for quantitative corrosion measurements. Some tools give a qualitative assessment of the internal diameter.

- Type 2

These tools measure the magnetic properties of the casing while logging, which allows a quantitative measurement of wall thickness. A quantitative measurement of casing ID is made simultaneously. In addition, it is possible to use this type of tool to detect corrosion damage in multiple casing strings. ^(4.66)

Neither type of tool is recommended for detecting small holes or isolated pitting. Its primary utility is for the detection of severe general corrosion or large holes. ^(4.65)

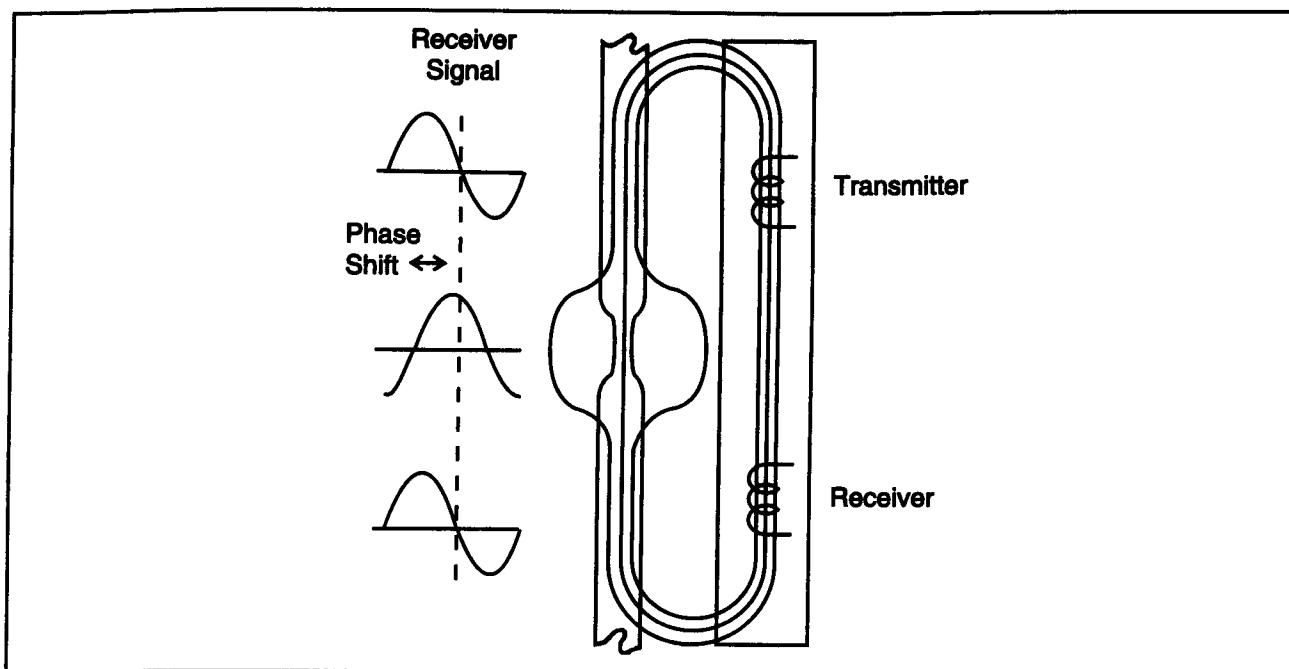


Figure 4.48 Schematic of Electromagnetic Phase Shift Measurement for Casing Thickness
(Courtesy Schlumberger)

Ultrasonic Scanning (Tubing and Casing)

Some ultrasonic tools measure only the ID of the tubing or casing, while others measure both casing thickness and casing ID, and can discriminate between internal and external damage. (Figure 4.49) The instrumentation consists of one or more ultrasonic transducers focused perpendicular to the pipe wall. ^(4.67)

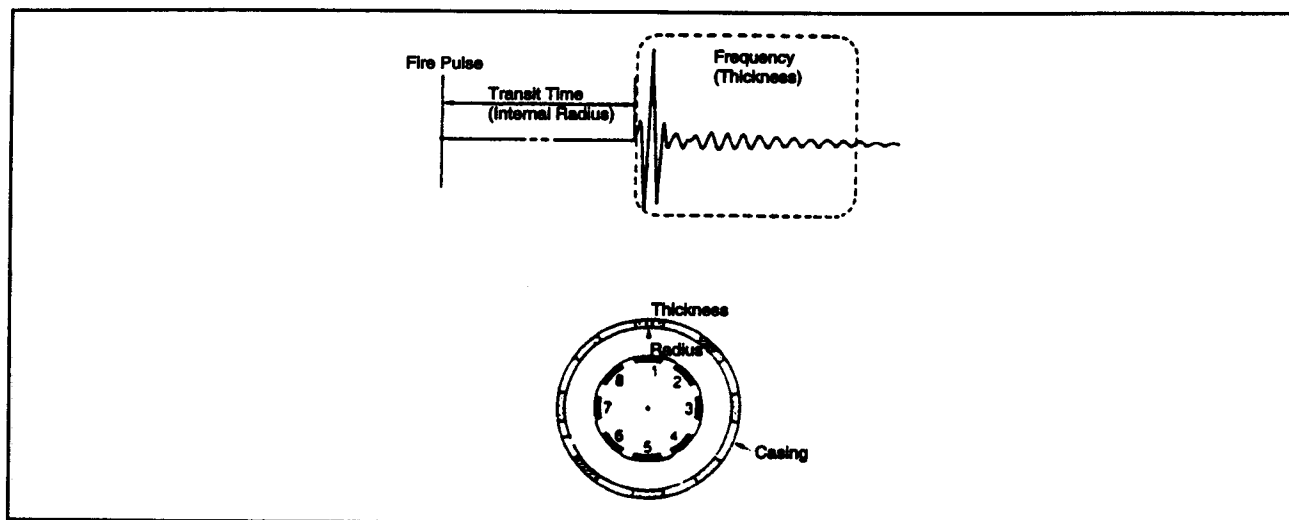


Figure 4.49 Ultrasonic Measurement of Casing Thickness and ID (Courtesy Schlumberger)

This type of tool works in either oil or water. Signal response is attenuated by gas, heavy mud, and scale buildup. While the caliper reflects reduction in diameter due to scale deposits, the thickness measurement responds only to metal thickness.

The accuracy of the dimensional measurements is typically 0.025 inches [0.6 mm].

Pipeline Inspection Tools

Pump-Through Inspection Tools

Inspection tools are available which can be pumped through a pipeline and will give a continuous record of pipe wall condition. They are often referred to as "intelligent pigs" or "smart pigs."

Use of these tools require that the pipeline be equipped with full-opening valves, and suitable pig launching and receiving facilities.

The minimum inspectable diameter is 4-6 inches, depending on the type of tool. Most tools require a minimum bend radius of 3D, although 5D may be required for the smallest diameters.

Careful cleaning is mandatory prior to any pig runs. This is especially true in produced-water or wet crude-oil lines, as wax buildup can impede an inspection tool's progress and affect its accuracy.

Magnetic-Flux-Leakage Pigs (MFL)

This type of tool measures wall thickness, and detects both internal and external corrosion. Some tools can differentiate between internal and external corrosion. ^(4.68)

MFL tools can be used in gas lines as well as in liquid-filled lines.

The magnetic flux leakage principle is described in this chapter under the heading of Downhole Inspection. A simplified drawing of an MFL inspection pig is shown in Figure 4.50, and Figure 4.51 shows the response of the magnetic field to a corrosion pit.

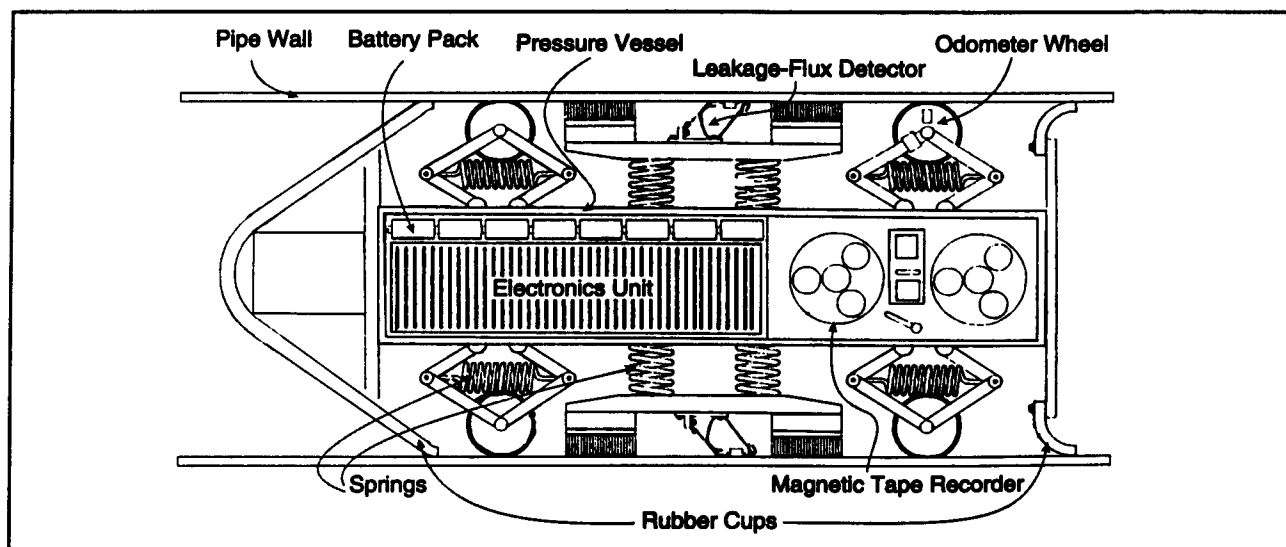


Figure 4.50 Simplified Schematic of MFL Pipeline Inspection Pig ^(4.69)

Ultrasonic Pigs (US)

Ultrasonic tools require that the line be filled with fluid in order to acoustically couple the ultrasonic transducers and the pipe wall. The liquid should be homogeneous in order to prevent scatter of the ultrasonic signal. Gas bubbles, oil droplets, or suspended solid particles can cause problems.

The ultrasonic wall-thickness tool utilizes the pulse-echo concept to detect metal loss. Non-contacting ultrasonic transducers are affixed to the tool body so that they remain a fixed distance from the

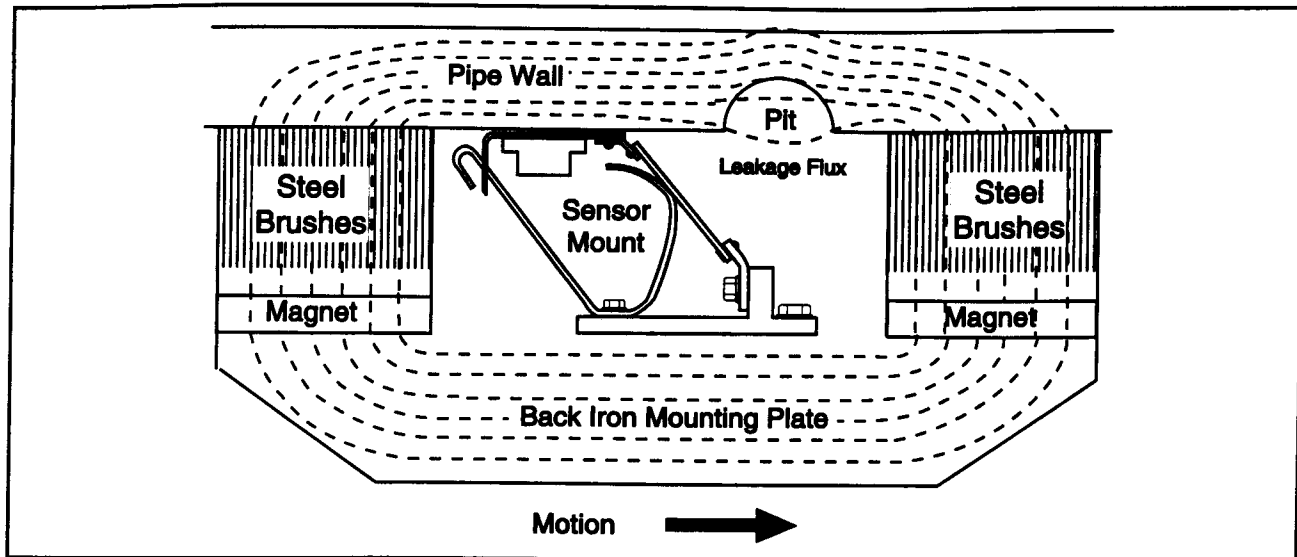


Figure 4.51 Pit Detection with an MFL Pipeline Inspection Pig^(4.69)

pipe wall as the tool travels through the pipeline. (Figure 4.52) An ultrasonic pulse of known velocity is transmitted through the liquid to the pipe wall. There are two echoes: the first arriving from the inside surface of the pipe and the second arriving from the outside surface.

Late arrival of the first echo represents loss of thickness from the inside wall (internal corrosion), while early arrival of the second pulse represents metal loss from the external pipe surface. ^(4.70)

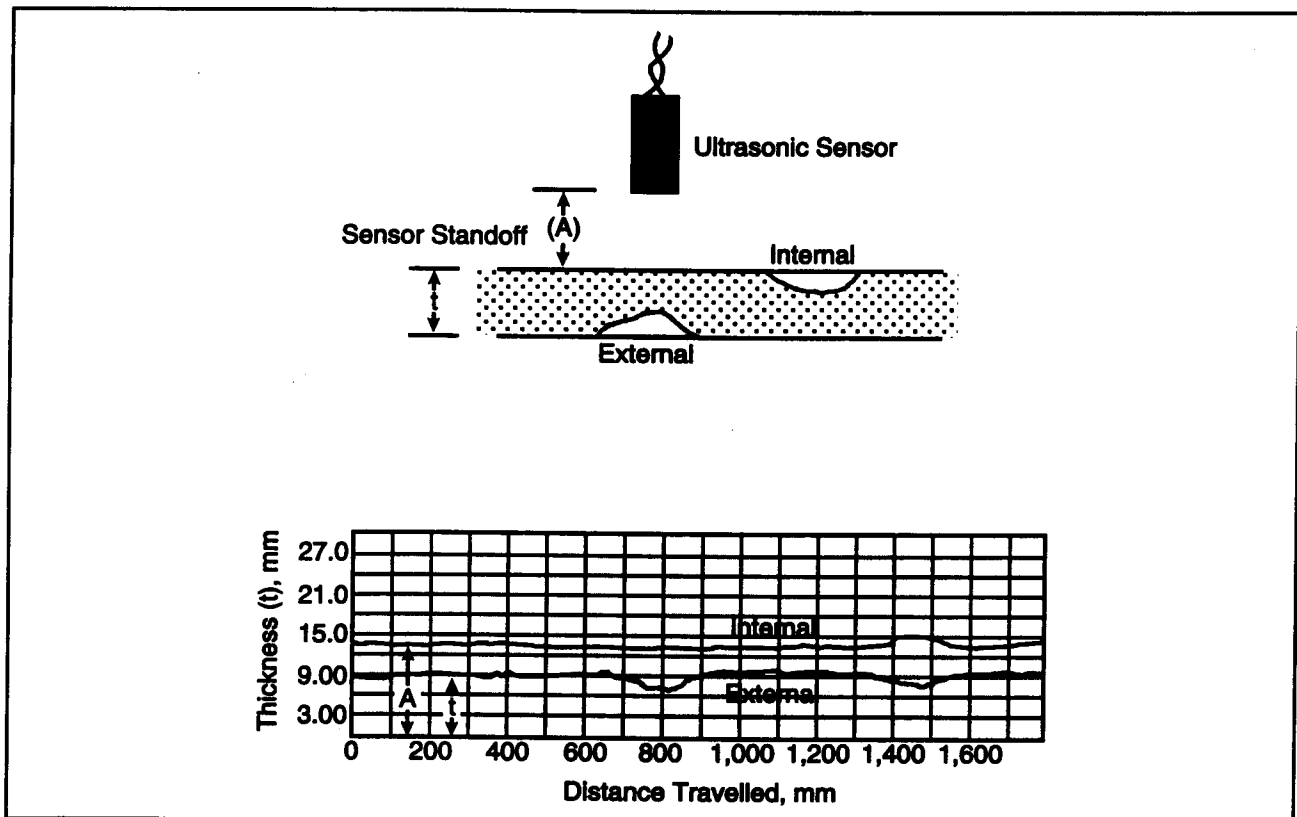


Figure 4.52 Pipeline Wall-Thickness Measurement with an Ultrasonic Pig^(4.70)

Wireline Tools

Also available are pipeline inspection tools which are pulled through a line with a cable or wireline. This approach makes smaller diameter tools possible, since the data processing and storage equipment do not have to be built into the tool. The data is transmitted through the cable to external data acquisition equipment.

The use of a cable limits inspection length to a little over a mile (2 km) with a copper wire.^(4.68)

Inspection of Surface Facilities

Ultrasonic Inspection

Ultrasonic devices are used to measure metal thickness and to detect defects in the metal.

The basic concept of ultrasonic inspection is to generate high frequency sound waves and transmit them into the material being inspected. These waves travel through the specimen until they encounter the opposite surface of the specimen or an internal discontinuity. Either an interface or a discontinuity will reflect the sound waves back to their origin where they can be detected. The time interval between transmission of the ultrasonic wave and the arrival of the reflected wave back at the point of transmission is proportional to metal thickness or the depth of the flaw. This method is called the pulse-echo technique.

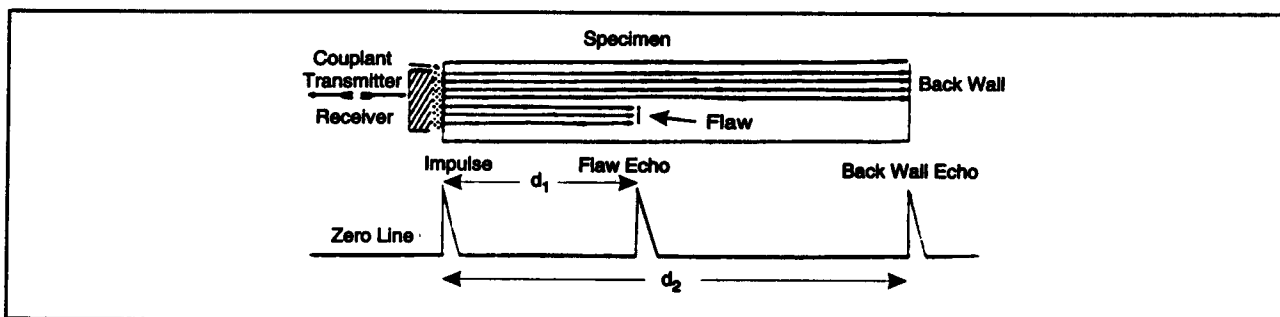


Figure 4.53 Pulse-Echo Ultrasonic Measurement Principle

The sound wave is both transmitted and received by a transducer, which contains two crystals made of piezoelectric materials such as quartz or a polarized ceramic. Piezoelectric materials will vibrate when subjected to a changing electrical field and will also produce an electrical potential when the material is placed under mechanical stress.

An electrical current is passed through one of the crystals, and it vibrates at a very high frequency (5-15 megahertz). This vibration produces ultrasonic sound waves, which are transmitted into the metal. This crystal is the transmitter.

The second crystal produces electrical current when struck by the reflected vibrations and acts as a sound wave receiver. (Figure 4.54)^(4.71)

Ultrasonic wall-thickness measurements are quite accurate on smooth, flat plates. (Figure 4.55a) However, it should be noted that serious errors can occur when attempting to measure the remaining wall thickness opposite corrosion pits because the signal is scattered by the irregular surface.^(4.63)

In the example shown in Figure 4.55b, the internal roughness scatters the signal such that insufficient energy returns to the transducer to give a reading.

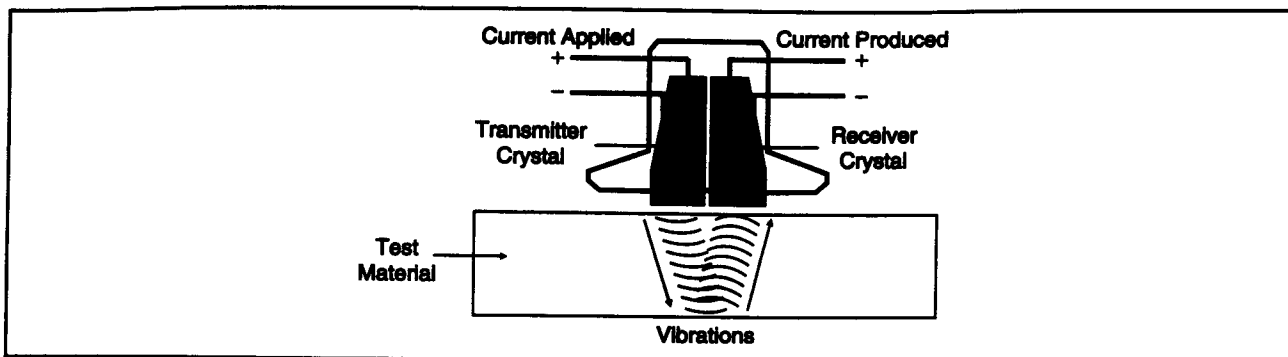


Figure 4.54 Ultrasonic Transducer^(4.71)

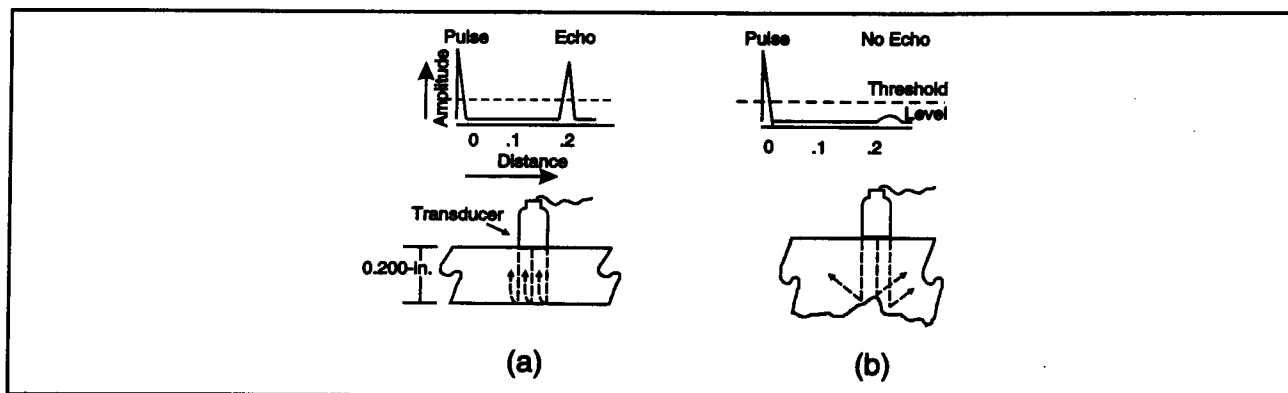


Figure 4.55 Ultrasonic Measurements^(4.72)

Radiography

Radiography is widely used for inspection of welds. It is also used for corrosion detection.

Either X-rays or gamma rays can be used, as they have similar wave lengths. However, gamma ray radiography is the most widely used method for field inspection. Gamma ray sources (iridium-192 and cobalt-60) are much smaller than X-ray machines and require no electrical power.^(4.73)

The process of radiography involves passing gamma rays or X-rays from a source, through the item being inspected, onto a piece of photographic film. When developed, the film is called a radiograph.

The amount of radiation which passes through a metal in a given length of time is inversely proportional to its thickness. This means that more radiation will pass through a thinned, corroded area than through a thicker, undamaged area. The photographic film becomes darker as it is exposed to increased amounts of radiation. Therefore, pits or corroded areas show up as dark spots or areas on a radiograph.

Radiographs are frequently taken in the horizontal plane to give a profile of the pipe walls. They can also be taken in the vertical plane to establish the pattern of attack on the bottom (or top) of lines or vessels.

Radiographic inspections can be carried out while equipment is in service.

Visual Inspection

To date there is no substitute for the human eye coupled with a modestly intelligent brain. Always utilize every opportunity to inspect. Any time a line is open, a pump is down, or a tank is being cleaned, get right in the middle of things and look. Use a camera, take notes, measure anything you can, and make drawings. This is the most reliable way of determining system condition.

Failure Analysis

Any time a failure occurs, go out, get nosy and conduct a postmortem. Use consulting or company laboratories if necessary and determine the cause of failure. Chances are you can avoid repetition of the failure if you can determine its cause.

A failure is your most expensive form of corrosion coupon. Use it wisely. Don't pinch pennies in analyzing it.

Equipment Records and Failure Reports

One of the most important things you can do is to keep accurate, up-to-date records. Know what you have done and when you did it. Once again, the idea is to keep track of your past performance (right or wrong) so that you can profit from it in the future.

Final Philosophy

Never rely on any single method of monitoring corrosion. Use several techniques simultaneously, if possible, and keep records with a passion!

A summary of corrosion monitoring techniques is presented in Table 4.9.

TABLE 4.9
Corrosion Monitoring Techniques

Method	Measures	Comments
Coupons	Average corrosion rate by weight loss. Pitting rate by pit depth measurement.	Must be positioned where corrosion is occurring.
Spools	Pattern of attack. Pitting rate by pit depth measurement. May be able to weigh.	Very useful in surface systems. Not as easy to remove as a coupon.
Linear Polarization	Instantaneous general corrosion rate.	Requires conductive fluid (water). May have problems in sour systems.
Potentiodynamic Polarization	Estimate pitting and general corrosion rates.	Used primarily for corrosion inhibitor evaluation.
Electrical Resistance	Change in electrical resistance of corroding element. Gives general corrosion rate.	Not normally used in sour systems due to conductivity of iron sulfide.
Galvanic Probe	Current generated by bimetallic couple.	Primarily used for O ₂ detection.

TABLE 4.9
Corrosion Monitoring Techniques (Cont'd.)

Method	Measures	Comments
Hydrogen Probe	Hydrogen generated by corrosion of probe. Rate of pressure increase is proportional to corrosion rate.	For sour systems. Must be temperature compensated.
Hydrogen Patch Probe	Hydrogen generated by corrosion of pipe wall. Gives hydrogen permeation rate.	Used only in sour systems.
Dissolved Gas Analysis	O ₂ , H ₂ S, CO ₂	Presence of H ₂ S in sweet system indicates sulfate reducing bacteria.
Corrosion Product Analysis	Indicates which dissolved gas is responsible for corrosion.	FeS will oxidize to iron oxide on exposure to air.
Dissolved Iron	Amount of iron dissolved by corrosion.	Not quantitative in sour or oxygenated systems. Must subtract any "natural" iron.
Inhibitor Concentration	Concentration of inhibitor present in fluid.	Helpful to determine inhibitor distribution in system.
Bacteria Counts	Number of bacteria present.	Related to corrosion rate.
Mechanical Calipers	Internal corrosion in tubing or casing. Pitting or general.	Scale or corrosion product may mask pits.
Electromagnetic Induction	Measures wall thickness and ID of casing.	Does not detect small holes or isolated pitting.
Ultrasonic Scanning	Measures ID in tubing and casing. Some tools also measure wall thickness.	Response is attenuated by scale buildup.
Magnetic-Flux-Leakage Pigs	Detects both internal and external attack in pipelines. General or pitting corrosion.	System must be built to accept tool. Reserved for large systems due to cost.
Ultrasonic Pigs	Measures both ID and OD of pipelines.	Line must be filled with liquid.
Wireline Pipeline Inspection Tools	Measures both ID and OD of pipelines.	Maximum inspection length is a little over a mile.
Ultrasonic Inspection	Thickness of metal. Presence of pits or cracks.	Very localized measurement.
Radiography	General or pitting corrosion.	Particularly useful in locating pitting corrosion in piping and wellheads.
Visual Inspection	Pattern and severity of attack.	Extremely reliable but often inconvenient.

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NOTES:

5

WATER TREATMENT MICROBIOLOGY

INTRODUCTION

Some knowledge of the behavior of microorganisms in water is extremely important since their presence can cause corrosion or plugging of equipment or the injection wellbore. They are simply another source of plugging solids or conditions which result in corrosion.

Biology can be defined as that branch of knowledge that deals with living organisms and their vital processes. Thus, in its broadest definition, it is that part of science which is concerned with the life processes of plants and animals.

Microbiology is one branch of biology which concentrates on microscopic forms of life known as *microorganisms*. Of primary concern in oilfield operations is the behavior of microscopic, single-celled organisms which are capable of living under all sorts of conditions and multiply with incredible speed.

Microorganisms Found in Oilfield Water Systems

Bacteria

Bacteria comprise the broad class of microorganisms of greatest interest to us in water handling.

The bacterial cell has little visible structure, even when examined with an electron microscope. Around the outside there is a cell wall which gives the cell its shape. Inside the cell wall is a thin semipermeable membrane which surrounds the contents of the bacterial cell and selectively controls the passage of substances between the cell and its external environment. The cell is filled with water containing different minerals and chemicals.^(5.1)

Most species are motile, meaning that the bacteria propel themselves through water by means of one or more whip-like flagella (singular: flagellum) which rotate and function like little outboard motors. A generalized diagram of a bacterial cell is shown in Figure 5.1.

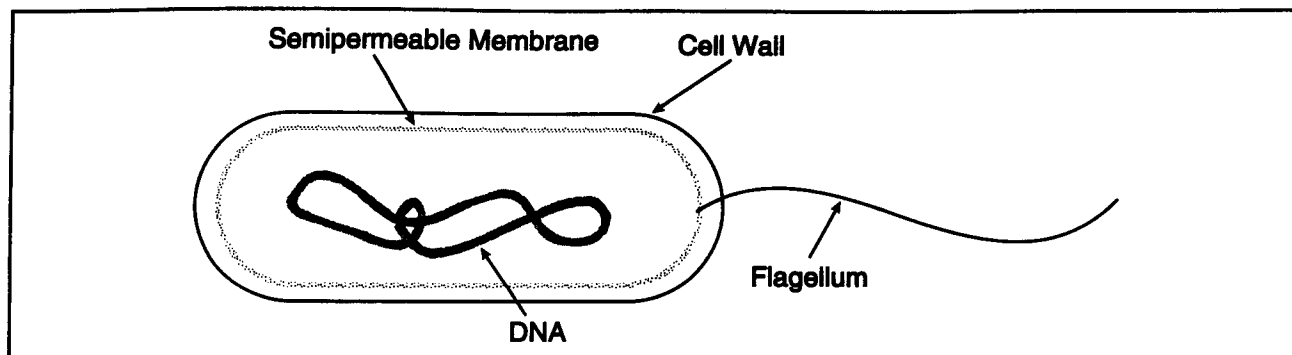


Figure 5.1 Generalized Diagram of Typical Bacterial Cell

Eucarya

This group of micro-organisms includes algae, fungi and protozoa.

Algae

Algae are single-cell plants which contain chlorophyll. Algae manufacture their food by photosynthesis using light as a source of energy and CO_2 as a source of carbon for all growth. They need sunlight for normal growth, although they can grow (slowly) in the dark.^(5.2)

Algae can form slime on the water surface which is easily identified by its green or blue-green color. It is often observed in stagnant water and in cooling towers.

Algae are present in seawater, although usually not as slimes. There are significant numbers in most oceans and they can contribute substantially to the plugging solids in the water, especially during algae "blooms" which occur at certain times of the year.

Fungi

Fungi generally grow better in aerobic systems and are thought to cause few problems in most water injection systems.

Protozoa

Protozoa are the simplest form of animal life. They are found in both fresh and salt water and require oxygen to live. In water injection systems they are found in open tanks or pits. They are also found in filters when the water is aerated. Generally, control of the other microbial population suffices to control the protozoan population.

Macro-Organisms

The oceans of the world contain creatures which are referred to as plankton. The term plankton is applied to all those animals and plants which live freely in the water and which, because of their limited powers of movement, just drift along with the water currents. This is not to say that they cannot swim. Some, such as crustacea and fish larvae, can swim very well, but they may not be able to swim faster than the water moves.

Plankton may be grouped by sizes. Very large animals such as jellyfish are called *megaloplankton*. Those organisms which are readily visible with the naked eye and down to a size which is retained by a net with 1 mm holes are referred to as "coarse net" or *macroplankton*. Organisms smaller

than 1 mm in size, but larger than 75 μm are *microplankton*. The smallest size is called *nanoplankton*. It includes tiny plants, bacteria, and creatures called flagellates. The smallest flagellates, that is those below 5 μm , are sometimes called *ultraplankton*.

Plankton are important to us because they make up a significant portion of the plugging solids in most seawaters. Also, they serve as food for larger creatures which may in turn contribute to plugging.

BACTERIA CLASSIFICATION

Bacteria may be classified in a number of ways. A description of some of the most common classification criteria follow.

Size And Shape

Bacteria are extremely small (about 0.5 μm in diameter) and exist in literally thousands of species. True bacteria are shaped like spheres, straight rods, or curved rods. The shapes are named as follows:

1. A single spherical bacterium: *coccus*

Several spherical bacteria: *cocci*

As a matter of interest, a string or chain of *cocci* is called a *streptococcus*, while a sheet or plane of *cocci* is called a *staphylococcus*.

2. Straight rod: *bacillus*
3. Curved rod:

Vibrio — single curve in the form of a “C”

Sigmoid — shaped like an “S”

Spirillum — two or more curves in the shape of a screw or spiral

Growth

The reason that bacteria can create so much trouble is that they can multiply with incredible speed. Some can double their population in 20 minutes under ideal conditions, which means that a single bacterium can become a thriving colony of millions of bacteria in a very few hours. A handful of slime from a water may contain as many bacteria as there are people in the world.

Bacteria can withstand an extremely wide range of temperatures (at least 14-210°F [-10 to 99°C]), pH values (about 0 to 10.5), and oxygen concentrations (0 to almost 100% oxygen).^(5.3) However, in water systems, they grow best in the pH range of 5-9 and at temperatures less than 180°F [82°C].^(5.4) They also prefer fresh water, but can do nicely in brines. They are extremely adaptable and hardy.

Bacteria can live either in groups or “colonies” attached to solid surfaces or suspended in water. Bacteria attached to a surface are called “sessile” bacteria. When they are suspended in water, they are termed “planktonic” bacteria, or sometimes simply “swimmers” or “floaters.”

The majority of bacteria are sessile. It has been reported that in a typical system, there are 1000 to 10 000 times as many bacteria attached to a surface as there are floating in the water.^(5.5)

It has also been shown that as sessile bacteria grow they produce a sticky substance called a *polysaccharide*, which the bacteria utilize to cement themselves to a solid surface. Continued

production of the polysaccharide results in the formation of a "biofilm" which surrounds and covers the bacteria. The biofilm can become quite thick (200-250 cells, and 1 mm in thickness).^(5,6) Within the layers of polysaccharide, there can be a whole community of bacteria. Cells of one species often exist in their own protected state beside cells of another, creating a mixed adherent population.

Oxygen Requirements

One method of classification of bacteria which is of interest in oilfield systems is whether or not specific bacteria require oxygen to live. They fall into three categories:

1. Aerobic bacteria — require oxygen to grow.
2. Anaerobic bacteria — grow best in the absence of oxygen.
3. Facultative bacteria — grow in either the presence or absence of oxygen.

BACTERIA WHICH CAUSE PROBLEMS

As previously stated, bacteria can contribute to both corrosion and plugging.

Bacteria can affect the corrosion process in oilfield systems in several ways. They can:

1. Generate hydrogen sulfide, thereby increasing the corrosivity of the water.
2. Produce organic acids that initiate or accelerate corrosion on the metal surface beneath the colonies.
3. Produce enzymes that can increase the corrosion rate by direct participation in the electrochemical corrosion process.
4. Oxidize soluble iron in the water, causing it to precipitate and form deposits (called "tubercles") that accelerate corrosion through the formation of concentration cells.
5. A combination of the preceding.

Plugging can result from bacterial activity due to the formation of bacterial biomass, the generation of corrosion product (such as iron sulfide) or the precipitation of soluble iron from the water.

Sulfate Reducing Bacteria (SRB)

Sulfate reducers probably cause more serious problems in oilfield injection systems than any other bacteria. They reduce sulfate or sulfite ions in the water to sulfide ions, resulting in H_2S as a by-product.

Four types of problems can result from sulfate reducer activity in an injection system:

1. They can participate directly in the corrosion reaction and cause pitting directly beneath the bacterial colony, as shown in Figure 5.2.
2. The generation of H_2S by bacteria can increase the corrosivity of the water. If the system is already sour, the additional H_2S generated by the bacteria may have little or no effect. However, if the system was originally sweet, the addition of H_2S to the system by bacterial activity can substantially increase corrosion rates and result in a pitting attack throughout the system.
3. The presence of sulfate reducing bacteria in a system which was originally free of H_2S creates the possibility of sulfide cracking and blistering of carbon steels.

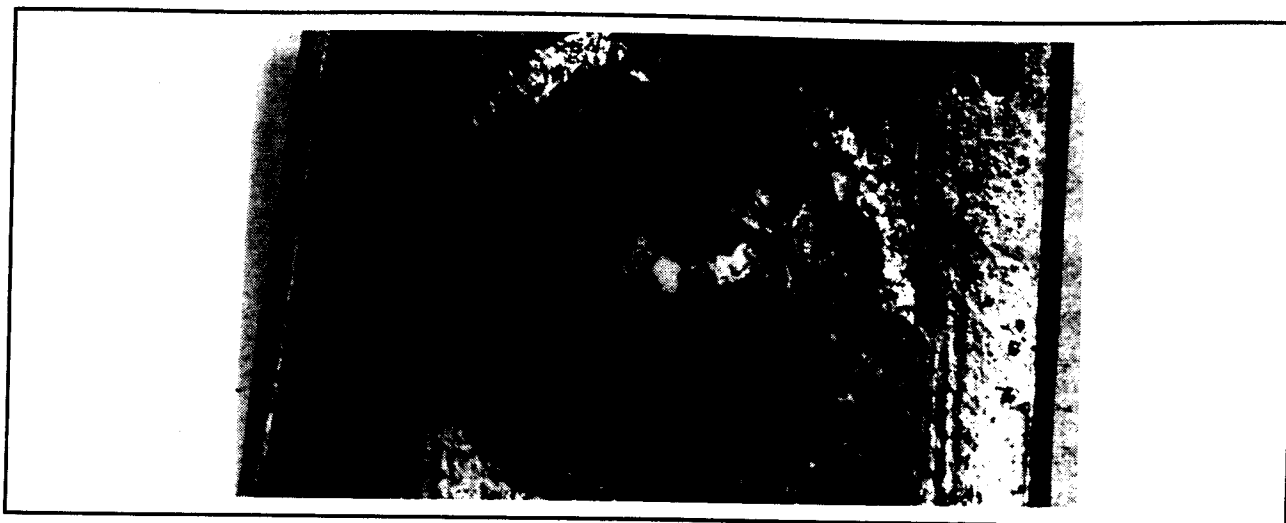


Figure 5.2 Corrosion Pit Beneath Sulfate Reducing Bacteria Colony

4. Sour corrosion results in the formation of insoluble iron sulfide which is an excellent plugging material.

Sulfate reducing bacteria are most likely to be found in stagnant or low velocity areas, and beneath scales or sludges. Common places for bacterial activity in injection systems are tanks, filters and the rat hole in injection and water source wells.

Types of Sulfate Reducing Bacteria

About nine families, or genera (plural of genus), of sulfate reducing bacteria are known. However, most SRB corrosion problems are attributed to members of two families: *Desulfovibrio* and *Desulfotomaculum*. Some of the species of each which are known to contribute to corrosion are listed in Table 5.1.^(5.7)

TABLE 5.1
SRB Families

Genus	Species	Shape
<i>Desulfovibrio</i>	<i>africanus</i>	Sigmoid rod
	<i>desulfuricans</i>	Vibrio
	<i>salexigens</i>	Vibrio
	<i>vulgaris</i>	Vibrio
<i>Desulfotomaculum</i>	<i>nigrificans*</i>	Rod
	<i>orientis</i>	Curved rod
*Formerly <i>Clostridium nigrificans</i>		

The sulfate-reducing organisms most commonly detected in the oilfield belong to the genus *Desulfovibrio*.^(5.9)

Desulfotomaculum can form spores. A bacterial spore is a structure formed within the body of a bacterium. Spores are resistant to temperature, acids, alcohols, disinfectants, drying, freezing, and many other adverse conditions. Spores may last for hundreds of years and then germinate in favorable conditions.^(5.3) A spore has many of the characteristics of a seed but is not a reproductive structure.^(5.8)

Effect of Salinity

Sulfate reducing bacteria are found in natural waters of all salinities from near zero to saturation.^(5.10) Many *Desulfovibria* are salt tolerant and can grow in NaCl concentrations as high as 100 000 ppm. Higher concentrations tend to limit growth.

Among *Desulfovibria*, two species have specific salt requirements. *Desulfovibrio salexigens* has an absolute minimum requirement of 25 000 ppm NaCl, while *Desulfovibrio vulgaris* is a fresh water strain requiring NaCl concentrations of less than 10 000 ppm.^(5.7)

Desulfotomacula are seldom found in waters containing more than 20 000 ppm NaCl. Above 20 000 ppm, the population is almost always *Desulfovibria*.^(5.10)

Temperature, Pressure and pH

Sulfate reducing bacteria as a group are reported to tolerate temperatures from 40-170°F [4-77°C], a pH range of about 5 to 9, and pressures of at least 14 500 psi [100 000 kPa].^(5.3) However, absolute values of temperature, pressure and pH required for the growth of sulfate reducing bacteria in natural environments are impossible to state with any degree of certainty. For example, sulfate reducers isolated from wells with bottom hole temperatures in excess of 250°F [121°C] have been cultured in the laboratory at lower temperatures, but would not grow at temperatures greater than 190°F [88°C] at atmospheric pressure.^(5.11) Furthermore, the maximum temperature at which sulfate reducing bacteria grow apparently increases with pressure.

The following statements apply to growth in the laboratory in artificial media:

- *Desulfovibrio*: The optimum temperature range for growth is approximately 77-110°F [25-43°C], with an upper temperature limit of 120°F [49°C].^(5.7)
- *Desulfotomaculum nigrificans*: The optimum temperature for growth is 130°F [54°C]. They exhibit slow growth at 150-160°F [66-71°C], and can survive at 170°F [77°C].^(5.7)
- *Desulfotomaculum orientis*: Exhibits optimum growth at temperatures of 85-100°F [30-38°C]. They are killed when the temperature exceeds 108°F [42°C].^(5.7)

Nutrition

Bacteria absorb their nutrients directly from the environment around them. Each cell contains proteins called enzymes that help break down nutrient molecules and enable the bacteria to extract energy from them.^(5.1)

A single living cell contains hundreds of different enzymes, each of which is an effective catalyst for a specific chemical reaction. However, the enzymes work together in a coordinated manner to produce the materials required for normal cell growth and metabolism.

Although all enzymes are initially produced in the cell, some are secreted through the cell wall and function in the cell's environment. This type of enzyme enables the cell to assimilate large molecules by breaking them down outside the cell into smaller molecules which can be absorbed through the cell wall.^(5.2)

Sulfate reducing bacteria require a number of nutrients in order to sustain growth. Some of the primary ones are:

- **Carbon.** Sulfate reducing bacteria are heterotrophic, meaning that all or most of their cell carbon is derived from organic substances and that they generate carbon dioxide when they

grow. They utilize organic materials dissolved in the water such as organic acids or alcohols as a source of carbon. Apparently they cannot utilize petroleum hydrocarbons^(5.10,5.12).

- **Nitrogen and Phosphorus.**
- **Dissolved Iron.** Sulfate reducing bacteria have an absolute requirement for relatively high concentrations of dissolved iron.^(5.10)
- **Sulfate, Sulfite, Bisulfite or Thiosulfate Ions.** Although the primary diagnostic character of sulfate reducing bacteria is that they grow with sulfate, reducing it to sulfide, they can also grow with sulfite and other reduced sulfur compounds.^(5.10)

A shortage of any of these materials can limit SRB growth.

The addition of oxygen scavengers or phosphorus containing compounds such as scale inhibitors could enhance growth if the concentrations of phosphorus or sulfate in the system are so low they are limiting growth. However, this is not likely, as most injection waters contain sufficient nutrients for an abundant growth of bacteria.^(5.8)

A source of nitrogen is rarely if ever a limiting factor on the growth of sulfate-reducing bacteria in waterflooding activities.^(5.8) Therefore, it is unlikely that nitrogen containing compounds such as corrosion inhibitors would stimulate bacterial growth.

Effect of Dissolved Oxygen and Hydrogen Sulfide

Sulfate reducing bacteria are found in oxygenated surface waters such as oceans. They are usually present in very small numbers and do not multiply at an appreciable rate. However, if the water is deaerated prior to injection, they then have an oxygen-free environment which is ideal for growth. Sulfate reducing bacterial activity is a common occurrence in deaerated seawater injection systems.

It is also possible to have growth in an aerated system with the assistance of aerobic bacteria. The aerobes establish themselves on the walls of the system and consume oxygen as they grow. An anaerobic environment is created beneath the aerobic bacteria, thereby providing an ideal breeding ground for sulfate reducers.

Hydrogen sulfide decreases the growth rate and can, at high concentration, slow the growth rate to zero. It is believed that the decreased growth rate is caused by a reduction of the dissolved iron concentration due to reaction with hydrogen sulfide and subsequent precipitation as iron sulfide.^(5.10)

Reservoir Souring

There have been a significant number of cases of "reservoir souring" due to sulfate reducing bacterial activity.^(5.13,5.14) In each case, the reservoir fluids are initially sweet. Injection of a sulfate-bearing water is initiated. Sometime after breakthrough of injection water in the producing wells, H₂S appears. The concentration gradually rises, and has been reported as high as 3100 mg/L in the gas phase.^(5.13)

In most cases, this phenomenon is associated with the injection of seawater. However, it has not occurred in every field where seawater has been injected. It has been reported in seawater floods in California, Alaska, and the North Sea.

The mechanism(s) by which reservoir souring occurs is not completely understood. However, reservoir contamination by thermophilic sulfate reducing bacteria in the injection water is considered to be the most probable explanation.

In shallow reservoirs the temperature is favorable for bacterial growth. However, even in deeper, hotter zones, the reservoir rock in the vicinity of the wellbore is cooled by the injection of large volumes of water, creating a favorable temperature regime for their growth.

Once established in the reservoir, sulfate reducing bacteria produce hydrogen sulfide which then travels with the injection water to the producing wells. Even if an effective biocide is being used, a 100% kill is unlikely, and once bacterial growth is established in a rock matrix, it is almost impossible to control with chemicals. This is due to the difficulty of contacting every square inch of surface area within the rock with adequate quantities of the chemical.

Zobell calculated that sulfate reducing bacteria could travel at between 2 and 40 feet per year through oil bearing sands.^(5.15) Therefore, although reservoir souring could occur in this way, one would not expect bacterial transport from the injection wells to the producing wells to be the primary cause of reservoir souring. Too many reservoirs have soured before bacteria traveling at these speeds could have reached the producing wells.

Bacterial contamination of the producing wells is also a possibility. However, it would be anticipated that this type of problem would be a more or less random event, and would occur in a few wells rather than throughout the entire field.

The net result of reservoir souring is increased corrosion, and more important, the possibility of sulfide stress cracking and/or hydrogen blistering in the production facilities. This makes it necessary to evaluate the probability of souring, and to select downhole tubulars for the producing wells and surface production equipment accordingly.

Iron-Oxidizing Bacteria

Iron-oxidizing bacteria are able to oxidize soluble ferrous ions in the water to form a sheath of ferric hydroxide around them as they grow. Examples of iron bacteria are *Siderocapsa*, *Gallionella* and *Sphaerotilus*. They are classified as aerobic bacteria, although they can apparently grow well with only trace amounts of oxygen (< 0.5 ppm).^(5.9)

Iron bacteria can cause both corrosion and plugging. Although they do not directly participate in the corrosion reaction, corrosion can result either from the activity of sulfate reducers under the hydroxide sheath or by the creation of an oxygen concentration cell.

Large numbers of iron bacteria can precipitate a sufficient quantity of ferric hydroxide to cause severe plugging problems. Iron bacteria are usually found in fresh waters but they may occur in brine.

Slime-Forming Bacteria

Slime-forming bacteria are a general class of bacteria capable of producing dense masses of slime on solid surfaces. Examples are *Pseudomonas*, *Flavobacterium*, *Enterobacter*, *Escherichia*, and *Bacillus*. They cause plugging and contribute to corrosion in the same ways as iron bacteria by shielding part of the surface. Slime can be expected in either brine or fresh water, in either aerobic or anaerobic systems. However, they are more common in low salinity aerobic systems.

Other Types of Bacteria

There are many other types of bacteria present in water injection systems which are not discussed here. The sulfate reducers, iron bacteria, and slime formers constitute the major sources of microbio-

logical problems, and some knowledge of their behavior will generally be sufficient to avoid serious microbiological problems.

CULTURING, IDENTIFYING AND COUNTING BACTERIA

Monitoring a system for bacterial activity entails sampling (which is covered in the following section), identification and counting of the bacteria.

Culturing Bacteria

Culturing bacteria is analogous to culturing flowers, potatoes, or green beans. The object is to make them grow. Bacterial culturing in artificial growth media is the standard technique for the estimation of bacterial populations.

A water sample thought to contain bacteria is placed in a liquid known as a "culture medium" which is a solution consisting of water and food that will make the bacteria of interest grow and multiply. In addition, many media contain a growth indicator. For example, culture media for sulfate reducing bacteria contain iron. When SRB's grow, they produce H_2S , which reacts with the iron to create an insoluble black precipitate, iron sulfide.

Different types of bacteria require different culture media, and some bacteria refuse to grow at all in artificial media. However, most bacteria of interest can be cultivated in a particular medium. The fact that media can be formulated in which only specific types of bacteria will grow makes it possible to identify the bacteria simply by noting the media in which growth occurred. Furthermore, by running the sample at several different dilutions, the number of each type of bacteria can be estimated.

The composition of the water used in the formulation of culture media may be arbitrary (e.g. 10 000 ppm NaCl) or it may be tailored to more closely match a specific water. There are several possibilities for the water used to make up the media:

- Use a sodium chloride solution which matches the chloride ion concentration of the water of interest.
- Make up a synthetic brine approximating the composition of the water.
- Use sterilized field water. This option is recommended when feasible. The water composition, including micronutrients, is as close to that in the actual system as possible.

There are many different versions of laboratory identification and counting techniques, but they will not be covered here.^(5.16) The general principles already outlined are followed with varying degrees of sophistication. API RP 38 describes a recommended method for examination of waterflood injection waters which is used by many laboratories.

Extinction Dilution Technique^(5.16-5.17)

This is a field technique, sometimes called serial dilution, which can be used to detect different kinds of bacteria. Detection of each class or type of bacteria requires a specific culture medium.

Sampling

Sampling procedures are covered later in this chapter.

Procedure

The extinction dilution procedure is illustrated in Figure 5.3 and is performed as follows:

1. Line up a series of serum bottles, each containing 9 mL of sterile growth medium. A 4 to 6 bottle series is common.
2. Inject 1 mL of the water sample into the first bottle and shake well. Throw the syringe away.
3. Withdraw 1 mL of solution from the first bottle with a new disposable sterile syringe and inject it into the second bottle. Shake the bottle. Throw the syringe away.
4. Withdraw 1 mL of solution from the second bottle with a new sterile syringe and inject it into the third bottle. Shake the bottle well and throw the syringe away.
5. Repeat this procedure until all bottles have been inoculated.

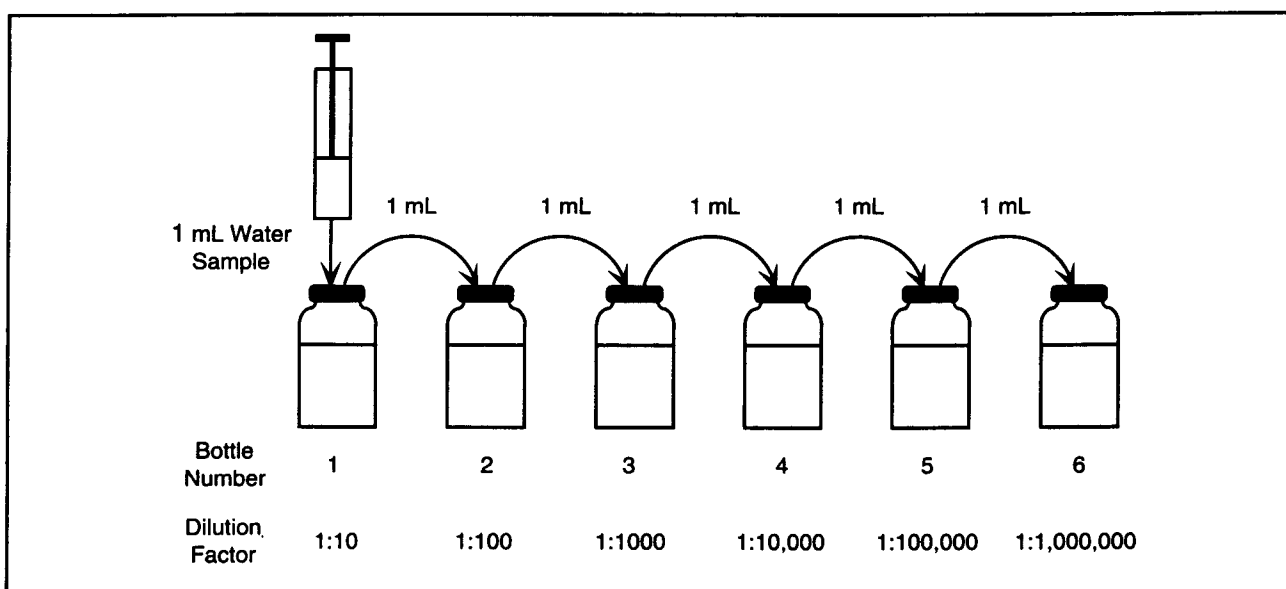


Figure 5.3 Extinction Dilution Technique

The point of this procedure is to dilute the sample to the point that the final 1 mL of solution that you inject into the last bottle has no bacteria in it; hence, the name extinction dilution technique. You have diluted the sample to the point of extinction of any bacteria present.

The fact that the dilution is performed in a series of fixed dilution ratios allows you to estimate the bacterial population of the original 1 mL water sample.

The rules of the game state that you cannot transfer part of a bacterium from one serum bottle to another. This means that when you withdraw 1 mL from a serum bottle containing 10 mL of liquid, there must be at least 10 bacteria in a bottle, or an average of at least one bacteria per mL, before a transfer is allowed. For example, if there were only 8 bacteria in the bottle, the average population would be 0.8 bacterium per mL, and transfer cannot occur according to the rules.

Similarly, if there are 15 bacteria in a bottle, the average population is 1.5 bacteria per mL. Since only whole-number transfers are allowed, a one mL withdrawal of liquid will net you 1 bacterium for transfer to the next bottle.

Additional examples are given in Table 5.2.

TABLE 5.2
Serial Dilution Examples

Series No. ⇒	1	2	3	4	5	6	7	8
Number of Bacteria								
Original 1 mL Sample	10	50	90	100	250	600	850	1000
First Bottle	10	50	90	100	250	500	850	1000
Second Bottle	1	5	9	10	25	50	85	100
Third Bottle	0	0	0	1	2	5	8	10
Fourth Bottle	0	0	0	0	0	0	0	1

Types of Cultures

In practice, two types of culture media are normally utilized and, therefore, two separate series of dilutions are run: one for sulfate reducing bacteria (SRB) and the other for general bacteria.

Sulfate Reducing Bacteria

The SRB series utilizes a growth medium which is specific to sulfate reducing bacteria. The bacteria counts obtained using this medium include *Desulfovibrio*. *Desulfotomaculum* may also be detected. However, if system conditions appear to be favorable to the growth of *Desulfotomaculum*, it may be desirable to inoculate an additional media designed especially for their detection as an additional precaution.

Commonly used media include those described in API RP 38, as well as a number of other media proposed by Postgate and others.^(5,9,5.10,5.16)

Once the bottles have been inoculated, they are set aside and allowed to "incubate" for a fixed time period. An incubation period of 28 days is recommended. However, shorter incubation periods may be used when it can be demonstrated that all growth occurs in less than 28 days.

A constant temperature is desirable during the incubation period and growth rates are temperature sensitive. The cultures should be incubated at a temperature within 9°F [5°C] of the recorded temperature of the water at the time of sampling if possible. If not, keep the temperature between 77°F and 100°F [25-38°C].

Growth is indicated when the bottle turns black. The SRB media contain soluble ferrous iron or a sterile iron nail. When SRB's grow, they produce H₂S which reacts with the iron to form insoluble, black iron sulfide.

General Bacteria Count

The "general" series employs a different growth medium which promotes the growth of "general" heterotrophic bacteria as well as facultative bacteria. An incubation period of 5 days is common.

The "general" count includes the general aerobic bacteria, primarily the slime formers, and can also include anaerobic bacteria as well as facultative bacteria. It does not include iron bacteria, which are difficult to culture in an artificial medium. They are usually detected by microscopic means.

Three types of media are in common use for the detection of general heterotrophic bacteria:

1. **Standard Bacteriological Nutrient Broth**

Growth is indicated by the development of turbidity. The turbidity is caused by the bacterial cells themselves, and is usually evident when the cell count exceeds 1 000 000 per mL.

2. Phenol Red Dextrose Broth

This medium contains sugar and phenol red, which is an acid-base indicator which turns from red to yellow when the pH of the culture medium drops below 6.6. When the sugar is fermented or oxidized by bacteria, various organic acids are produced. The resulting acidity causes the pH to drop, which causes the color of the medium to change from red to yellow.^(5,9)

Growth is indicated by a color change from red to yellow, the development of turbidity, or both. Turbidity indicates general bacterial growth, and a color change indicates the presence of acid-producing bacteria.

3. Thioglycolate Medium.

This medium is used to detect anaerobic heterotrophic bacteria. Growth is indicated by the development of turbidity.

Once the bottles have been inoculated, they are set aside and allowed to "incubate" for 5 days at the same temperature as the SRB bottles.

Final Count

As a rule of thumb, growth will usually occur within 3 days for general bacteria, but two weeks to a month may be required for sulfate reducer growth. The bottles should be examined daily for signs of growth and the results recorded. The final reading for general bacteria should be taken after 5 days, and the final count on the SRB's should be taken after 28 days unless experience indicates that shorter periods are acceptable.

Interpretation of Results

The number of bacteria present in the original 1 mL of water injected into the first bottle can be estimated using Table 5.3.

TABLE 5.3
Bacterial Growth Interpretation

Bottle Showing Growth	Dilution Factor	No. of Bacteria Indicated (Bacteria/mL)	Number of Bacteria Reported (Bacteria/mL)
1	1:10	1 to 9	10
2	1:100	10 to 99	100
3	1:1000	100 to 999	1000
4	1:10,000	1000 to 9999	10,000
5	1:100,000	10,000 to 99,999	100,000
6	1:1,000,000	100,000 to 999,999	1,000,000

For example, if bottles 1, 2, and 3 show growth, but bottles 4 through 6 remain clear, then the water contains 100-999 bacteria per milliliter, and a count of 1000 per mL is reported. If only one bottle shows growth, and the rest remain clear, then the water contains 1-9 bacteria per milliliter, and a count of 10 bacteria per mL is reported.

Common Growth Interpretation Problems

There are a number of common occurrences which can interfere with interpretation of the results obtained using the serial dilution technique. Some of the more common ones are:

1. All Bottles Show Growth

If all bottles show growth, then it is not possible to estimate the population. For example, if all 6 bottles in a series are positive, you would have to report the population as "equal to or greater than 1 000 000 per mL."

2. Immediate Positives

A point of caution: If the first bottle of SRB media turns black within 2 hours after the one mL water sample has been injected into the bottle, it is not the result of bacterial growth in the bottle. They grow pretty fast, but not that fast. The black color is iron sulfide resulting from high levels of H_2S in the water sample reacting with dissolved iron in the bacterial culture medium.

If blackening of the first bottle occurs within 2 hours, one of the following courses of action is common:

- a. Proceed with the serial dilution. Bottles 2 through 6 will usually remain clear and can be used to detect growth. Set them aside for observation as usual.
- b. Collect at least 50 mL of water in a sterile bottle and add an Alkaseltzer tablet. The Alkaseltzer will strip most of the H_2S from the sample. When the tablet has stopped fizzing, remove one mL of water with a sterile syringe and perform the serial dilution as usual.

Similarly, if the first bottle of general media turns turbid (or yellow in the case of the phenol red indicator) within one hour of inoculation, this is not due to bacterial growth, but is the result of natural turbidity in the water or an excessively low pH which causes the color change.

3. Bottle Skipping

Sometimes one of the bottles in the middle of a series remains clear while bottles on either side of it show growth. If this occurs, the skip should be noted, and the number of bacteria corresponding to the highest numbered bottle in the series which showed growth should be reported.

For example, assume that growth is indicated in bottles 1, 2, and 4, while bottles 3, 5 and 6 remain clear after being incubated for the required time period. There are a number of possible explanations for this event, including accidental contamination of bottle 4. However, you seldom know why it occurred, and have to simply make the best of a questionable situation. In this example, if you are reasonably confident that the bottles are numbered properly, you should report 10 000 per mL, and note which bottle was skipped.

Significance of Results

This method permits the estimation of the number of *planktonic bacteria* floating in the water. Since most of the bacteria in a system will be *sessile bacteria* attached to solid surfaces, it is a very poor way to assess the number of bacteria actually living in the system. Nevertheless, it is a simple test to perform, and has proven to be a very useful indicator of the level of bacterial activity.

Often the absolute number of bacteria in a given water sample is less important than *changes* in population. If the number of bacteria increases as you move across the system from the water source

to the injection wells, active bacterial growth within the system is almost certain. Similarly, increased bacterial counts with time at any given point in the system is a good indicator of active growth.

1. General Count

Bacterial counts of less than 10 000 organisms per mL are not considered significant in untreated waters. As a rule of thumb, a count of 100 000 per mL indicates a strong possibility of plugging and a need for biocide treatment. Start examining injectivity for any decrease and look for any evidence of increased injection pressures or filter plugging.

Some slime forming bacteria will only grow on a solid surface and will not be detected by this technique.

2. Sulfate Reducing Bacteria

The presence of a single sulfate reducing bacteria is considered to represent a *potential* problem.^(5.16) Remember that SRB are sessile bacteria and that this method only detects planktonic bacteria. Hence, the odds are very high that there are many bacteria clinging to the wall of the system for every one which is floating in the water.

Conversely, low bacterial counts do not necessarily mean that there is no bacterial problem. They may be so securely established under deposits that very few bacteria are dislodged from the sessile community, resulting in low counts in the water.

Other evidence of the severity of the problem are H₂S levels and "black water" due to iron sulfide in the water.

Once sulfate reducing bacteria are detected, they should be monitored very closely, and treatment should be instituted if bacterial counts and or H₂S levels increase.

Rapid Bacterial Detection and Counting Methods

Culturing techniques rely upon growth of bacteria for their detection. Bacteria may be present in a given sample, but if they do not grow in the selected artificial media, they go undetected. In addition, growth takes time, and the use of culturing as a bacterial detection and counting technique is not quick.

There are a number of methods which allow one to rapidly gather information about microbial populations in oilfield systems. They directly detect bacteria or enzymes which are associated with particular types of bacteria.

Some of the more common rapid assessment techniques are summarized in the following paragraphs. For a more complete summary, see NACE TM0194, *Field Monitoring of Bacterial Growth in Oilfield Systems*.^(5.19)

Microscopic Examination

Microscopic techniques are extremely useful to trained microbiologists. For example, iron and slime bacteria can be identified quickly with a phase-contrast microscope. However, it is often difficult to distinguish bacteria from suspended solids.

Fluorescence Microscopy^(5.20)

One way to make bacteria stand out from their surroundings is to treat them with a fluorescent dye, or "stain," which will make them fluoresce when exposed to UV light of the proper wavelength. They can be easily distinguished from non-living particles of similar size and shape by looking at them

through a microscope under UV light. This technique is called fluorescence microscopy allows direct counting of bacteria within a very short time.

Cells are usually concentrated by filtration through a polycarbonate membrane filter, which will retain the cells on a flat surface rather than in the mesh surface of cellulose acetate membranes (the ones usually used to collect suspended solids for TSS determinations).

Cell Stains

Total cell counts can be obtained using stains which combine with cell material present in both living and dead bacteria. Common stains used for this purpose include acridine orange, and DAPI (4, 6 diamidido-2-phenylindole).

The total number of *living cells* can be determined using FDA (fluorescein diacetate) stain.

Antibody Stain

The fluorescent dye is bound to antibodies which will seek out *sulfate-reducing bacteria* cells. Consequently, only those bacteria recognized by the antibodies will fluoresce under the microscope. The major advantage of the method is speed, as results are obtained within two hours.

The major limitation of the method is that the antibodies are specific to the type of SRB used in their manufacture. However, a large number of SRB antibodies can be combined to make the test fairly general. The method detects both living and dead cells.

Unfortunately, in addition to requiring trained personnel, microscopic techniques are not practical for routine use in the field.

ATP Photometry(5.20,5.21)

ATP analysis provides a means for rapidly determining the quantity of *living organisms* present in an injection water. It is not specific to bacteria, but since the majority of the organisms present in many oilfield waters are bacteria, it can be a very useful technique. It is particularly helpful in the evaluation of biocide treatment programs.

The basis for the method is as follows:

1. ATP (adenosine triphosphate) is present in the cells of all living organisms.
2. ATP is destroyed within 20 seconds of cell death through release of ATP-destroying enzymes.
3. The amount of ATP per cell is a linear function of cell volume, e.g., twice the cell volume results in twice as much ATP.

ATP analysis is a method of measuring the amount of ATP present in a given sample. This enables a quantitative measurement of the amount of living organisms in the sample. The method is based on the fact that ATP will react with a mixture of luciferin and luciferase in the presence of oxygen to produce light (bioluminescence). The amount of light emitted from the reaction is measured with a photometer and the number of organisms determined from calibration data.

A summary of the procedure is as follows:

1. The water sample is filtered through a 0.45 μm pore size membrane filter. Bacteria and other organisms are thus removed from the water and retained on the filter surface. This concentrates the organisms, thus increasing measurement sensitivity. Also, it is required when the water contains NaCl (as in the case of most oilfield waters) because *NaCl inter-*

feres with the ATP-luciferin/luciferase reaction. It should be noted that sulfide also interferes with the reaction.

2. The ATP must then be quickly extracted from the cells prior to its destruction by enzymes soon after cell death. Several methods are available, but a common method is to drop the membrane filter into a boiling solution of 0.05 molar tris hydroxy nitromethane buffer solution. The heat destroys the ATP-destroying enzymes, preventing their interference. It also kills the bacteria and causes them to burst and release their cellular contents, including ATP, into the buffer solution.
3. Luciferin/luciferase is then added to the buffer solution and the emitted light measured with a photometer. The number of bacteria present is then obtained from calibration data.

ATP analysis has one overwhelmingly positive feature: it provides a very quick indication of the total planktonic bacterial activity in a system. You don't have to wait through long incubation periods to get results as in the case of conventional culturing techniques. However, it does not identify the type of bacteria present.

As previously stated, the presence of a few sulfate reducing bacteria can cause trouble, whereas a general count of 10 000 bacteria per mL can usually be tolerated. Therefore, if ATP analysis were to indicate a total count of 5000 bacteria per mL in a particular sample, this would be acceptable providing none were sulfate reducers. However, the situation would be quite different if 2000 of those bacteria were sulfate reducing bacteria! Because of the need to specifically identify sulfate reducers, it is common to use conventional culturing techniques to determine their population in conjunction with ATP analysis as a rapid means of measuring total bacterial activity.

Enzyme Determinations^(5.20)

Hydrogenase Measurement

The test is used to detect the presence of the hydrogenase enzyme. This enzyme is produced by bacteria which are able to use hydrogen as an energy source.

Hydrogen is generated at the cathode in many corrosion reactions. The utilization of this hydrogen by bacteria such as SRB depolarizes the cathode and accelerates the corrosion reaction. Therefore, the presence of hydrogenase indicates the presence of bacteria which can accelerate the corrosion reaction by cathodic depolarization.

Hydrogenase testing is usually performed using sessile samples. The sample is exposed to an enzyme-extracting solution, and the degree of hydrogen oxidation in an oxygen-free atmosphere is indicated by a color reaction with a dye.

A response can be expected in 30 minutes to 4 hours. A 12-hour exposure is generally used for comparison purposes. The test can be carried out in the field or laboratory.

APS-Reductase Measurement (RAPID CHECK)

This method is based on the functional definition of sulfate-reducing bacteria, which includes any bacteria capable of anaerobically reducing sulfate to sulfide. A unique requirement for this process is the presence of an enzyme, APS-reductase. Since this internal enzyme is common to all SRB's, measurement of its concentration in a sample permits the estimation of the total number of SRB present.

The test requires about 20 minutes and can be carried out in the field or laboratory using commercially available test kits. The lower limit of detection is typically about 1000 cells/mL, although sensitivity can be increased by concentrating the sample.

Water Sampling for Bacterial Analysis

Samples are taken for the determination of both the planktonic and sessile populations. Sampling the water to determine the number of planktonic bacteria present is by far the most common practice.

Sampling Points

Sample the following points in an injection system:

1. Water Source

The wellhead, pond, stream, lake, ocean, or produced water.

2. Vessels, Tanks and Filters

Sample both the inlet and outlet, as well as the backwash discharge on filters.

3. Injection Wells

Sample at several injection wellheads located at various distances from the injection plant.

Sampling for Planktonic Bacterial Analysis

The sampling technique is basically the same as described in an earlier chapter. However, there are some additional requirements:

1. If a sample container is used, it should be initially sterile, or free of bacteria.
2. The use of a plastic or rubber sampling hose which has been previously used is discouraged, as it is a possible source of contamination. You don't want to contaminate the sample and find a bacterial problem which doesn't really exist in the system.
3. Sample in such a way that oxygen is excluded when culturing sulfate reducing bacteria.
4. An alternate procedure for collecting a water sample is to insert the tip of the syringe directly into the stream of water flowing from the sample valve, then immediately inoculate the first bottle of media. This method is ideal for on-site analysis.

Timing

The water sample should be injected into the growth media or subjected to other analysis immediately after sampling. Changes in the bacterial population occur rapidly and old samples can give a false picture of the population in the water system.

Sulfide Concentration

Sniff the sample for H_2S , then measure the total sulfide concentration. If the water entering the system is sweet, but becomes sour somewhere in the system, this is a very good sign that sulfate reducers are the source of the H_2S .

Also note the color, clarity and amount of suspended solids. Severe SRB problems often cause the water to turn black due to the formation of iron sulfide.

Sampling Sessile Bacteria

Robbins Device

The Robbins Device was developed at the University of Calgary by Robbins and Costerton as a means of estimating the population of sessile bacteria in a water system.^(5.22) The basic concept of the

device is to insert small, sterile, mild steel coupons or "studs" through the wall of a piece of 1/2-inch diameter pipe such that the face of the studs are flush with the internal pipe wall. In effect, they become a part of the pipe wall and furnish a site for the growth of sessile bacteria. A sidestream of water from the system is flowed through the device, and after a given exposure period, the studs are removed, and the number of bacteria on each stud is evaluated by one of several methods.

Commercial biological probes based on the principles of the Robbins Device are marketed by several vendors. These probes consist of a holder containing five to eight, small, mild steel studs or coupons. The probe is available in two versions:

- High Pressure Access Systems

This type of probe contains either five or six studs and is designed for connection to a high pressure access fitting.(Figure 5.4) This enables the probe to be installed and retrieved without depressurizing the system by using one of the high pressure access systems discussed in Chapter 4.

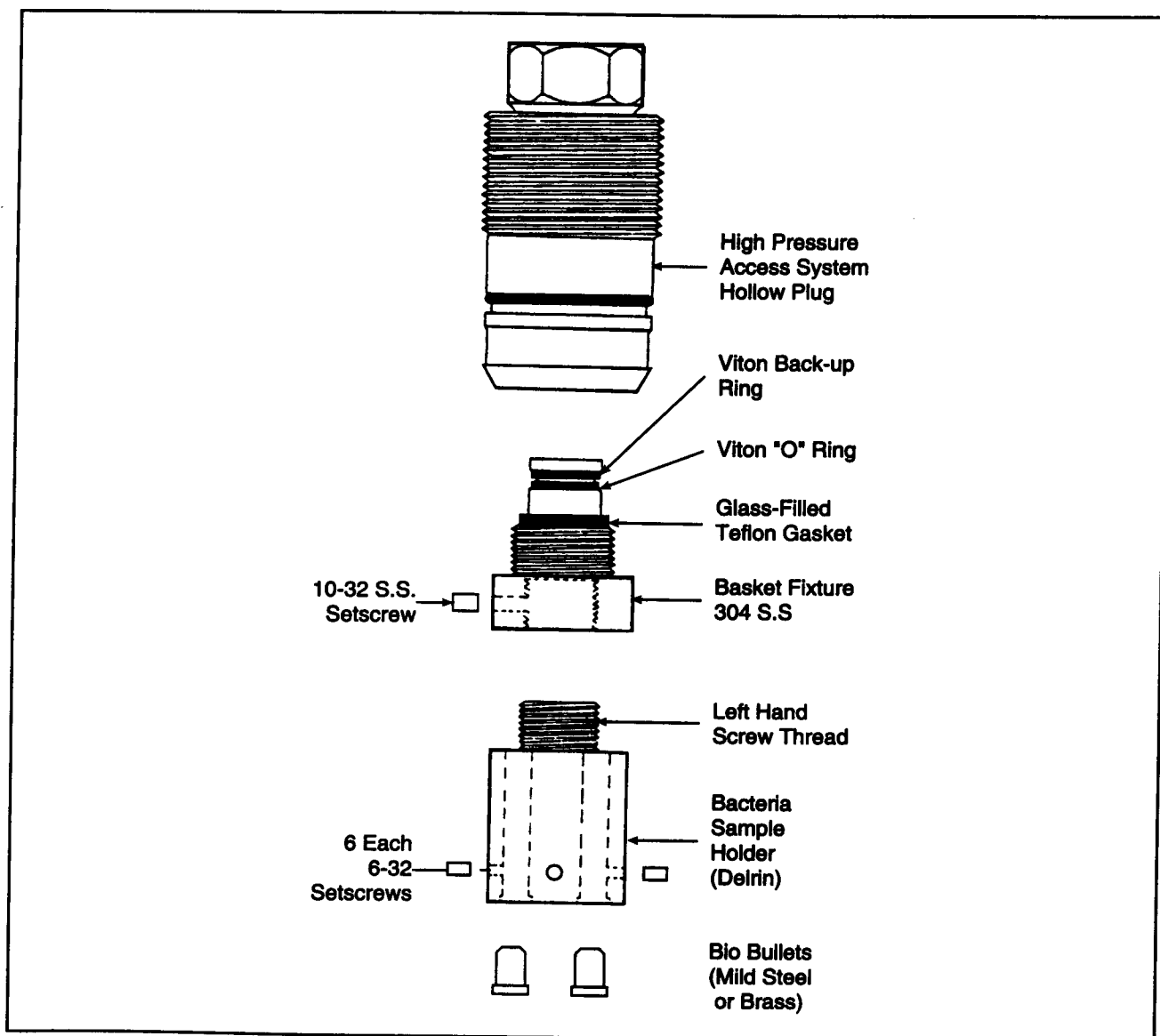


Figure 5.4 Cortest Biological Sample Probe Assembly

- **Low Pressure Systems**

The probe contains eight studs and is attached to a two-inch threaded plug. The portion of the system where the probe is located must be isolated by valves and depressured for probe insertion and removal.

The general procedure for using a biological probe is as follows:

1. Sterilize the studs by soaking in ethyl alcohol, and insert into the plastic holder with sterile tweezers. (Don't touch the studs!)
2. Install the probe in the system, preferably on the bottom of a line at the 5 or 7 o'clock position.
3. After the desired exposure period (typically 2-6 weeks) remove the probe from the system and quickly extract the desired number of studs. Be careful not to contaminate the studs. Don't touch them!
4. Determine the number of bacteria attached to the surface of each stud. Three methods are in common use:
 - a. Each stud is placed in a plastic test tube containing a special solution and glass beads. The bacteria are then dislodged from the stud by placing the test tube on a vortex mixer or by vigorous hand shaking for two minutes. A portion of the solution is then removed and the bacterial content evaluated by the ATP or serial dilution methods.
 - b. The second technique involves scraping the biofilm from the stud surface with a sterile scalpel blade. The scrapings, the stud, and the blade are placed in a special solution, which is then put in an ultrasonic cleaning device. A sample of the solution is then evaluated by serial dilution or ATP methods.^(5.22)
 - c. The bacterial population on a stud surface can also be determined by direct examination using fluorescence microscopy.

Use of Solids Scrapings

It is often desirable to scrape scale or solids from the pipe wall or from a pit and examine it for the presence of bacteria.

Culturing can be carried out using media in bottles equipped with screw-on caps. A consulting laboratory or chemical company should be contacted for help in the event you decide to culture scale samples.

Direct examination of solids can be carried out using some of the rapid bacterial and detection methods previously discussed.

CHEMICAL CONTROL OF MICROORGANISMS

Types of Chemicals

Chemicals used for bacterial control can be broadly classed in several ways.

Function

1. **Bactericide:** A chemical which kills bacteria.
2. **Bacteriostat:** A chemical which inhibits or retards growth of bacteria.

3. Biocide: A chemical which kills other forms of life in addition to bacteria. A more universal killer.
4. Biostat: A chemical which retards or inhibits the growth of other life forms in addition to bacteria.

Chemical Composition

Inorganic Chemicals

Chlorine

Chlorine is the most widely used inorganic biocide for water injection systems. Its use is confined to surface waters such as seawater and fresh water from supply wells. Its use is covered in a subsequent section of this chapter.

Chlorine Dioxide

Chlorine dioxide (ClO_2) is used as a bactericide in industrial waters.^(5.2) It is typically generated on-site by mixing either sodium chlorate (NaClO_3) or sodium chlorite (NaClO_2) with hydrochloric acid to produce ClO_2 and has successfully been used in oilfield systems.

It can also be created by reacting sodium chlorite with chlorine.

It is a powerful oxidizer and reacts with sulfides in water to form sulfates.

The primary concerns with the use of chlorine dioxide are its corrosivity to steel and the possibility of creating a combustible mixture when it comes in contact with crude oil.^(5.23) These concerns have limited its use as a biocide in production operations.

Organic Chemicals

Aldehydes, quaternary ammonium compounds and amines are common examples of organic bactericides. Most bactericides sold by chemical companies, other than chlorine, are organic.

Aldehydes

Glutaraldehydes are very widely used for bacterial control in the oilfield. Acrolein is also used, but much more rarely. (See Chapter 6 for more information on Acrolein) Formaldehyde is rarely used because of concerns about its role as a carcinogen.

Aldehydes are not very good at penetrating biofilms and are often blended with other chemicals such as quaternary ammonium compounds to increase their penetration efficiency.

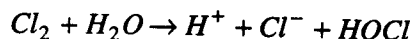
"Quats" and Amines

Quaternary ammonium compounds and quaternary phosphonium compounds are commonly referred to as "Quats." They are very surface active and effectively act as detergents. Their use is limited to waters with fairly low salinity such as seawater and fresher.

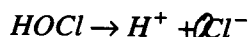
Amines are quite similar to quats. They are very surface active. When applied continuously they behave as corrosion inhibitors.

Chlorination

Chlorination is very widely used because it is one of the least expensive and most effective bactericides. When added to water, chlorine hydrolyzes to form hypochlorous and hydrochloric acids:^(5.15)



The hypochlorous acid then ionizes to form hydrogen ions and hypochlorite ions:



Effect of pH

The degree of ionization is dependent on pH. Below a pH of 5, molecular chlorine is present. Above this pH, HOCl and OCl⁻ are the species present. The relative percentages are shown as a function of pH in Figure 5.5.

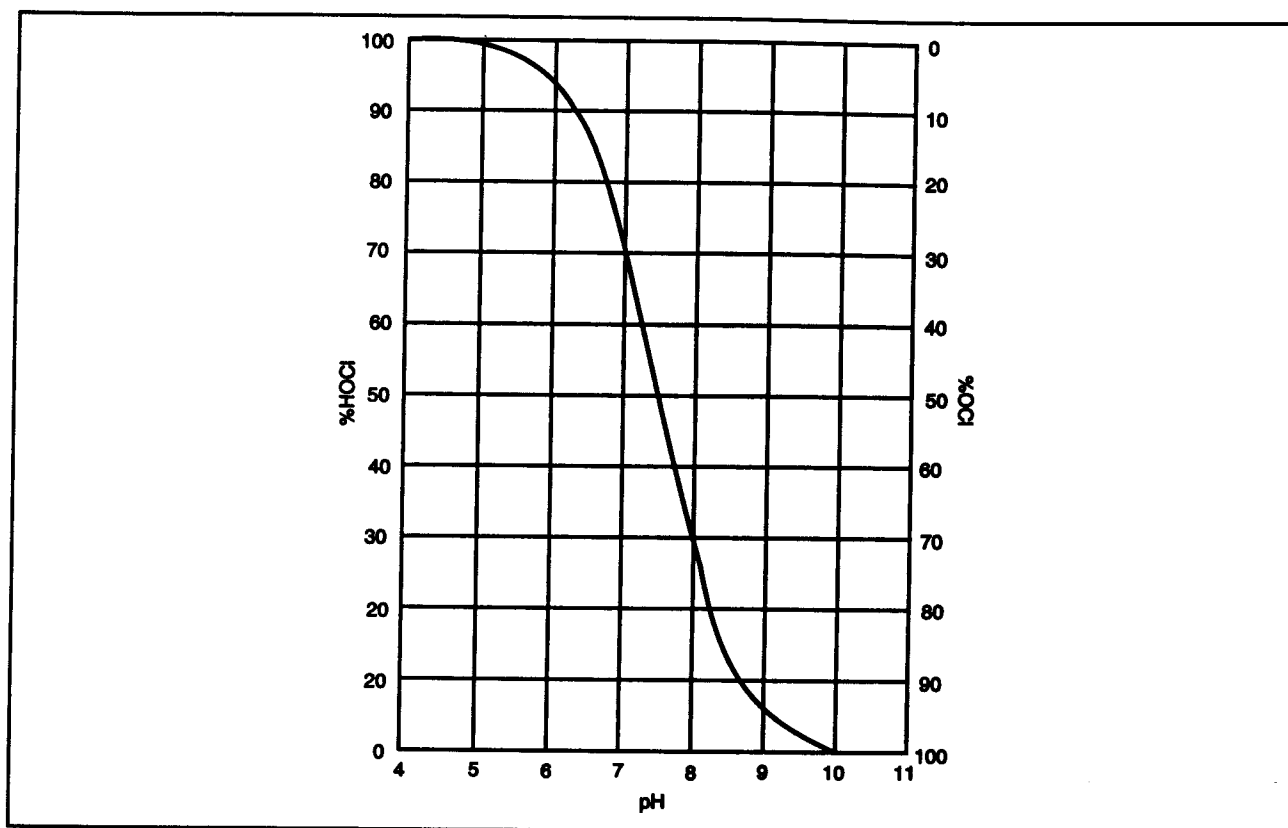


Figure 5.5 Effect of pH on the Concentration of Hypochlorous Acid^(5.24)

The effectiveness of chlorine depends on which of these species are present and is therefore a function of pH. For instance, the killing power of HOCl is much greater than that of OCl⁻. Hence, the higher the pH, the less effective a given quantity of chlorine. It is only 1 to 10% active at a pH of 8-9. However, in waters containing bromide ions (such as seawater), chlorine oxidizes the bromide ions to form HOBr, which is still an effective biocide at pH 8-9.

The amount of chlorine required to effect a kill is a function of time and temperature as well as pH. The rate of kill increases with temperature and decreases with pH.

Some typical data showing the relationship between pH and the chlorine residual required for a 10-minute kill is shown in Table 5.4.

TABLE 5.4
Required Chlorine Residual

pH	ppm
6-8	0.2
8-9	0.4
9-10	0.8

The chlorine residual or "free" chlorine is the total amount of chlorine present as Cl_2 , HOCl , and OCl^- .

Continuous injection of chlorine should be sufficient to maintain a chlorine residual of 0.2-0.5 ppm at the injection wellhead.

Chlorine Demand

Since chlorine is a very strong oxidizing agent, it reacts with many materials. Once it reacts it is no longer available to kill bacteria. Hence, it is necessary to establish how much chlorine will be used up by reaction with other materials in order to establish the total amount of chlorine needed. The amount used up by the system is called the chlorine demand. The amount of chlorine which must be injected to kill bacteria is:

$$\text{Chlorine Required for Bacterial Control} = \text{Total Chlorine Injected} - \text{Chlorine Demand}$$

Some of the things which react with chlorine are:

1. Ferrous Iron

One ppm chlorine will oxidize 1.6 ppm ferrous iron (Fe^{++}) to ferric iron (Fe^{+++}).

2. Hydrogen Sulfide

Chlorine will react with H_2S as previously mentioned in Chapter 4.

3. Organic Compounds

Chlorine will react with some corrosion inhibitors and scale control chemicals.

4. Sulfite Ion

Chlorine will react with the sulfite oxygen scavengers. This is covered in Chapter 6.

This means that the use of chlorine is limited if there is a lot of H_2S or ferrous iron to cope with in the system.

Chlorine is not normally used in systems which have long, bare steel injection lines. If the line is several miles long, it will be necessary to inject large quantities of chlorine in order to obtain a residual of 0.2-0.5 ppm at the end of the line due to the loss of chlorine by reaction with the steel. This can result in increased corrosion rates as well as increased treatment costs.

Compatibility

The compatibility with any other chemicals to be used in the system must also be checked. In the case of oxygen scavengers, either of two approaches may be followed:

1. The chlorine may be added a sufficient distance *downstream* to permit the oxygen scavenging reaction to go to completion prior to reaching the chlorine injection point.
2. If chlorine is to be injected *upstream* of oxygen scavenger injection, additional scavenger must be injected so that there will be enough present to react with both the chlorine and the oxygen. Since this results in removal of the chlorine, it is necessary to inject chlorine or some other biocide downstream of oxygen scavenging if a biocide is required in the downstream portion of the system.

Forms of Chlorine

"Chlorine" is available in several forms. However, from the standpoint of bacterial control, it really doesn't matter which one you pick, since all will form the same relative amounts of Cl_2 , HOCl and OCl^- once added to the water, depending on the pH.

Liquid Chlorine

Liquid chlorine is supplied in steel cylinders ranging in size from 105 lbs to 1 ton. The chlorine vaporizes as it leaves the cylinder and is added to the water as a gas with a chlorinator. A typical vacuum operated, solution feed chlorinator is shown in Figure 5.6.

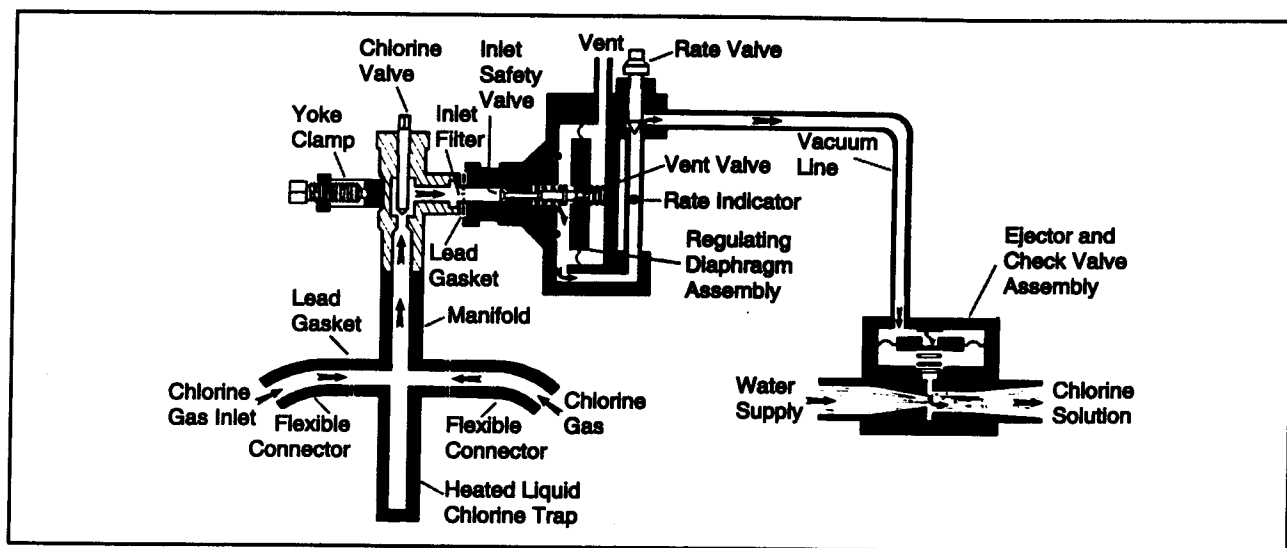


Figure 5.6 Flow Diagram of a Gas Chlorinator (Courtesy Capital Controls)

Water flowing through the ejector at high velocity creates a vacuum which opens a spring-opposed diaphragm check valve in the ejector body. When the check valve opens, a vacuum is transmitted to the vacuum regulator, causing the diaphragm to open the chlorine inlet valve. Chlorine gas passes through the flow meter and rate control valve to the ejector, where it mixes and dissolves in the water.

Caution: Chlorine is very poisonous and must be handled with care.

Hypochlorite Generators

Hypochlorite (OCl^-) can be produced in chloride-containing waters by electrolysis. The brine is passed through a special electrolytic cell called a hypochlorite generator, which contains two electrodes, an anode and a cathode. An impressed DC electrical current flows from the anode to the cathode,

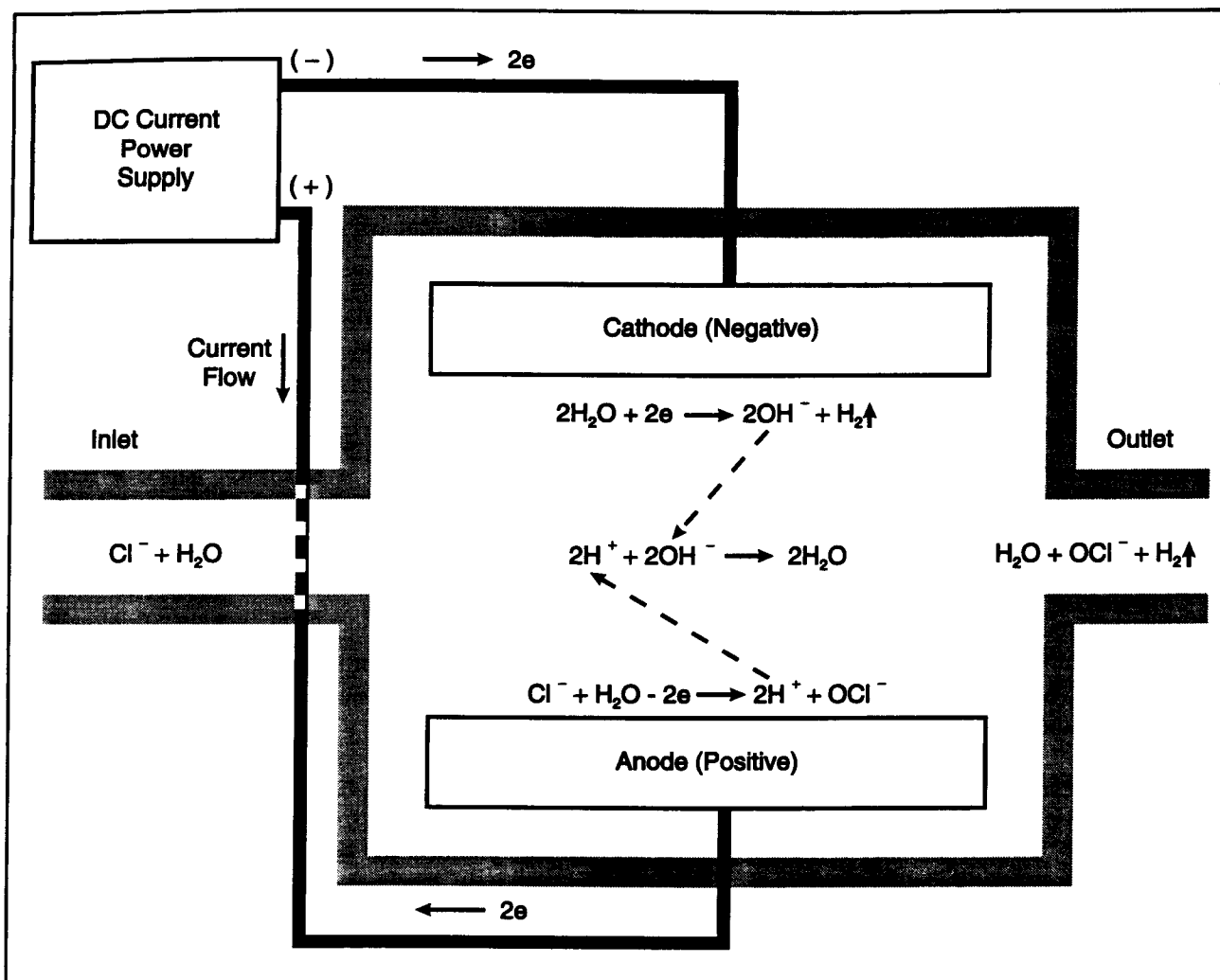


Figure 5.7 Chemical Reactions in a Hypochlorite Generating Cell

through the brine. Hydrogen ions are converted to hydrogen gas at the cathode and chloride ions are converted to OCl^- ions at the anode as shown in Figure 5.7.

The OCl^- solution/ H_2 gas mixture leaving the generator is usually passed through a gas-water separator to separate the hydrogen gas from the hypochlorite solution prior to its addition to the water system. The hydrogen is separated and vented for safety reasons, since the lower limit of flammability for hydrogen in air is 4.1%.^(5.25)

Hypochlorite generators are commonly used in seawater systems to eliminate the need for transporting and storing liquid chlorine.

Hypochlorite Solutions

Liquid hypochlorite solutions such as sodium hypochlorite or calcium hypochlorite are available and can be injected with a conventional chemical pump. They are seldom used because of their high cost relative to the other sources of chlorine.

Chemical Selection and Evaluation

Chemical selection for bacterial control is analogous to the selection of a chemical for the control of corrosion or scale.

First the problem (the type of bacterial problem) must be identified, then chemicals chosen which will deal with it effectively. On-site time-kill testing of different bactericides is recommended as an initial step in chemical selection.

Several items must be considered in selection:

Kill or Control?

The decision whether to use a bactericide or a bacteriostat is dictated by the type of bacteria involved. Sulfate reducers require a bactericide, since a total kill is desired. Since a reasonable number of slime formers can be tolerated without serious problems, a bacteriostat is often used for their control.

"Resistant Strains"

We often hear about the development of "resistant strains," which become resistant to a particular biocide. This seems to infer genetic mutation which results in the evolution of a bacteria which is extremely difficult to kill. In practice, this is not thought to occur.

The apparent creation of a "resistant strain" is evidenced by the fact that a given biocide gradually ceases to be effective. The most common explanation is often referred to as "selective adaptation." This simply means that certain members of the bacterial population are easily killed by a given biocide, while other types of bacteria are not. Over a period of time the bacteria which are resistant to the biocide gradually become dominant in the bacterial community, and the effectiveness of the chemical treatment declines.

This phenomena does not always occur. However, because it is possible, it is usually a good idea to select a minimum of two biocides. Then, if a given chemical starts to show decreased effectiveness, alternating treatment with a second, generically-different chemical will usually solve the problem.

Bacteria do not develop an immunity to chlorine.^(5.3) However, at normal treating concentrations, chlorine has limited power to penetrate deposits and organic masses, and may not be effective in dirty systems. Effectiveness can often be improved by the injection of an appropriate surfactant along with the chlorine.

Compatibility with Water and Other Chemicals

Make sure that the chemical is compatible with your water. Some will precipitate or "salt out" in higher brines. Also, compatibility with oxygen scavengers and corrosion or scale inhibitors must be established.

Time-Kill Tests

It takes time for any bactericide to kill the bacteria present. Therefore, it is wise to determine what length of time is necessary for a particular chemical to do its job at several chemical concentrations. A specific method for sulfate reducers is spelled out in NACE Standard TM0194.^(5.19)

It is important to know the time-kill relationship, especially where batch treatment is utilized.

Treatment Method

The treatment method must also be considered. If the bactericide is to be continuously injected an initially high concentration is usually required to bring the bacterial population under control; then lower chemical concentrations can usually be effective once the bacterial population has been brought under control.

If batch treatment is to be used, a high concentration slug is periodically pumped through the system, and the object is a total kill. Here the concentration, slug size and contact time can be initially sized by time-kill tests, then adjusted by actual experience.

In most cases, organic biocides are injected on a batch basis because of improved cost-effectiveness over continuous injection. Also, selective adaptation is more likely when bacteria are exposed to continuous, low-level concentrations than when subjected to periodic high concentration shocks.

Since immunity is not a problem with chlorine, it is usually injected on a continuous basis. Concentrations are kept as low as possible in order to minimize any increased corrosivity, as well as for economic reasons.

Chemical Application

Clean the System

The first rule of successful use of bactericides is to clean the system. A thorough cleaning job is necessary and has only one purpose: to remove all obstacles between the bactericide and the bacteria. No chemical can kill bacteria if it cannot contact them! ^(5.4)

1. Clean out the injection lines and tubing as outlined in Chapter 3, using solvents, acid and line scrapers if necessary.
2. Open all tanks, vessels and filters, and manually clean out all accumulated sludge and scale.
3. Backflow all injection wells. If the wellbores are plugged with bacterial deposits or slimes, a strong oxidizing agent such as sodium hypochlorite is normally used to attack them. In order to achieve maximum effectiveness, the sodium hypochlorite is usually followed by hydrochloric acid.

The sodium hypochlorite solution kills bacteria and completely dissolves the polysaccharide biofilm. ^(5.3) The acid dissolves any acid-soluble inorganic material and neutralizes the basic sodium hypochlorite solution. This prevents the precipitation of compounds from the formation water which are less soluble at basic pH values, such as calcium carbonate.

Sodium hypochlorite solutions are quite corrosive and must be inhibited prior to use. In tests conducted by Dowell, exposure of N-80 tubing to an uninhibited 5% sodium hypochlorite solution at 175°F [80°C] and atmospheric pressure resulted in a corrosion rate of 664 mpy. ^(5.26) However, inhibitors are available which will reduce the corrosion rate to acceptable levels.

In systems where large diameter lines run for several miles it is highly advisable to install permanent pigging facilities and pig the lines on a regular basis. This act alone will help to decrease bacterial problems by removing deposits and at least part of the biofilm. If the line scraper is followed by a batch of biocide, the effectiveness of the biocide is greatly increased due to the fact that the chemical can readily contact the remaining biofilm. This normally results in a substantial reduction in chemical costs.

Of course, bactericides contain a certain amount of detergency. If the system is not too dirty, there may be enough detergency to clean up the system. However, this is seldom true and a systematic cleaning operation prior to initiation of treatment is strongly recommended.

Also, remember that if you rely strictly on the detergency of the chemical, try to prevent the solids which may be washed loose from being injected into the formation. This can be accomplished by installation of wellhead cartridge filters.

Eliminate Stagnant or Low Velocity Areas

Examine the possibility of eliminating stagnant or low velocity areas by changes in system design. Since bacteria grow more rapidly in slowly moving or stagnant waters, system modification to minimize the number of low velocity areas will make bacterial control an easier task.

Sterilize the System

Once the system has been cleaned, it should be "sterilized." This means that the bacteria must now be killed. A high concentration slug of bactericide, with sufficient residence time to kill the bacteria, is used. Don't forget that this means the lines, tanks, filters and injection wells. However, it also means the water source. This frequently involves producing wells if produced water is used.

Institute Treatment

At this point "normal" treatment, either continuous or batch, can be instituted. The chemical should be added as near to the water source as possible. It should be added in an area where good mixing is possible.

Injection into the water intake line (surface waters), down the annulus of the supply well, or just downstream of the supply pump are common locations.

Evaluation of Chemical Treatment Programs

As in any other situation, the ultimate question is whether or not the chemical(s) selected actually works in your system. This can only be determined by closely monitoring the system.

A good monitoring program will include some combination of the following procedures, carried out across the system on a regular schedule:

1. Inspection of the chemical injection points to ensure that the chemical is the one you selected, and that it is being injected into the system at the proper concentration.
2. Estimation of specific families of planktonic bacterial population in water samples using serial dilution or other culturing methods.
3. Estimation of total planktonic population in the water using ATP or Fluorescence Microscopy.
4. Estimation of the sessile bacterial population using a Robbins Device for collection, ATP or Fluorescence Microscopy for estimation of the total population, and culturing to identify the types of bacteria.
5. Measurement of H_2S concentrations.
6. Visual examination of the water and suspended solids measurements.
7. Internal inspection of the system for deposits and corrosion.

It should be emphasized that you may be able to kill the planktonic bacteria, yet fail to kill the sessile bacteria which are actually doing the damage to the system. When this happens, it is typically due to the presence of scale, corrosion products, or deposits shielding the bacteria from the chemical, and/or the inability of the chemical to penetrate the biofilm.

The success of a treating program should be judged not only by a decrease in the bacterial population, but also by a decrease in leak frequency, plugging, and suspended solids, coupled with increased water clarity.

ULTRAVIOLET RADIATION

It is well known that ultraviolet light will kill bacteria. It halts growth by producing chemical alterations in the cell which prevents it from dividing. However, commercial ultraviolet units capable of treating large volumes of water were not available until the mid 1980's.

When water containing bacteria flows through an ultraviolet light unit, the probability of killing a given bacterium is dependent on the length of time the cell is exposed to the ultraviolet light and the intensity of the light reaching the cell. The intensity reaching the cell will depend upon:

1. The output of the lamp(s), which is usually measured in milliwatts/cm².
2. The distance from the UV light source to the bacterium.
3. The nature and amount of suspended matter in the water. Undissolved particles will scatter some of the UV light, thereby reducing the amount penetrating the water.
4. Any material dissolved in the water which can absorb ultraviolet energy will reduce the intensity. Films can build up on the quartz windows between the water and the UV lamp and reduce light intensity. Quartz windows are used because quartz is transparent to the ultraviolet wave lengths.

A typical dose-response curve is given in Figure 5.8. The dosage is expressed as milliwatt-seconds/cm², which is the product of the output of the lamp (milliwatts/cm²) multiplied by the exposure time in seconds. The relative kill is expressed both as the surviving fraction, which is the number of surviving cells divided by the original number of cells, and as the percent survivors.

Results given for one field test demonstrated a 99.9+% kill of sulfate reducing bacteria. Furthermore, it was stated that the cost of using ultraviolet light was significantly less expensive than using a biocide treatment in the case reported.^(5.27)

Ultraviolet light units are intended to prevent entry of planktonic bacteria into a particular portion of a system by killing them as they are carried through the unit in the water. Any bacteria that escape death in the UV unit will be free to multiply in the system, since there is no residual effect from the radiation. Therefore, it is likely that some form of chemical treatment will still be required in most systems where UV radiation is utilized.

It should be noted that the use of ultraviolet light is limited to clean waters containing very small amounts of suspended solids and little if any dissolved or suspended oil, due to the ability of these materials to reduce the ultraviolet light intensity transmitted through water.

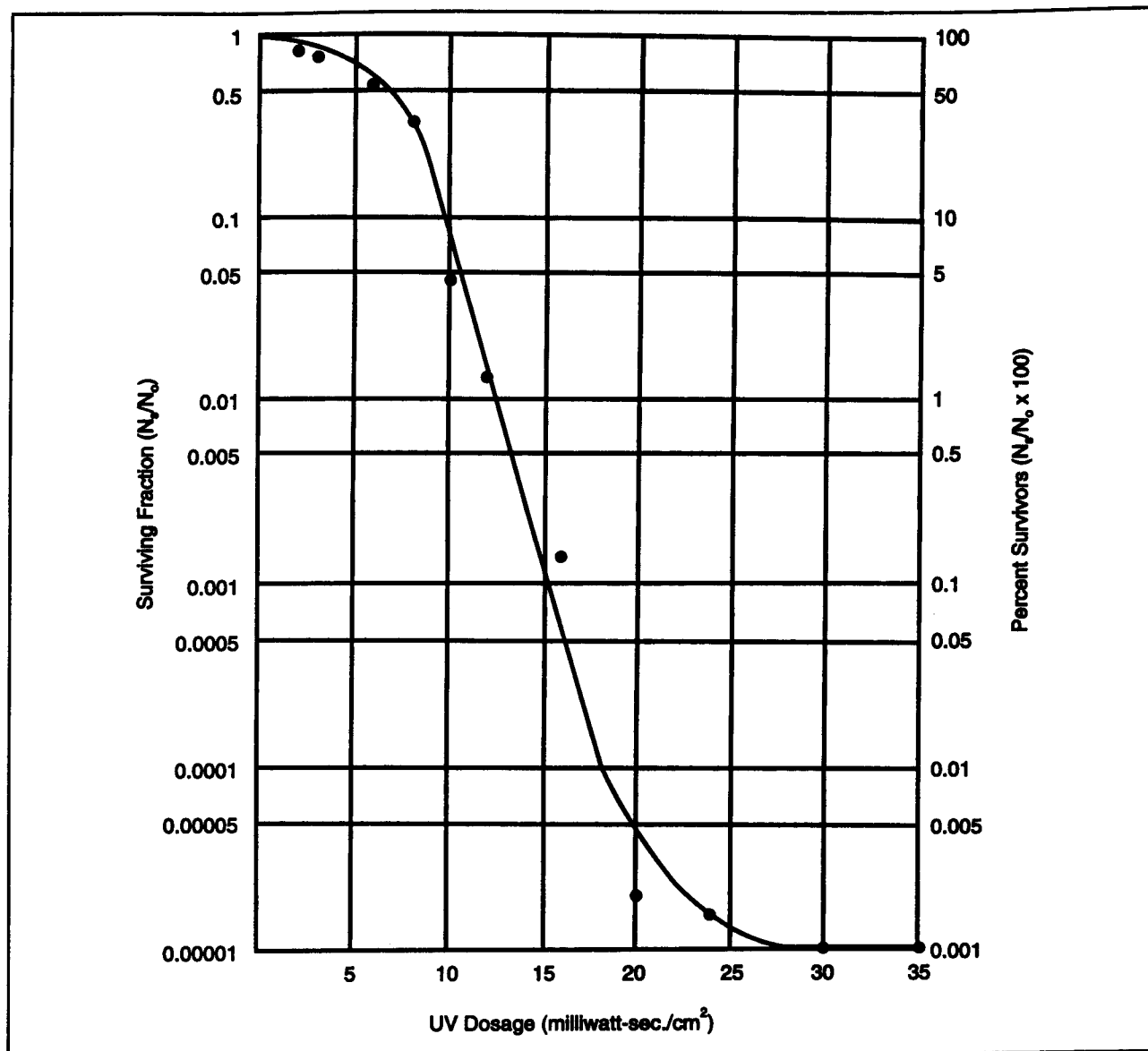


Figure 5.8 Typical Ultraviolet Light Dose-Response Curve for a Bacterium^(5.27)

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6

WATER PROCESSING TECHNOLOGY

Injection waters are processed to remove dissolved gases, suspended particles or dispersed oil. Water softening equipment is used to treat water for certain enhanced recovery processes and for boiler feedwater.

DISSOLVED GAS REMOVAL

It is often desirable to remove dissolved gases such as O_2 , H_2S or CO_2 from water to reduce its corrosivity. The concentration of a gas dissolved in water can be reduced to a few parts per billion by mechanical means. However, chemical removal is required to reach a value of zero.

Mechanical Removal Theory

The mechanical removal of any gas from solution is governed by three factors.

Dalton's Law of Partial Pressures

The total pressure exerted by a gas mixture is the sum of the pressures exerted by the individual components.

$$P_T = P_1 + P_2 + P_3 + \dots + P_n \quad (6.1)$$

The partial pressure of a particular component in a gas mixture is equal to the mole fraction of the component present in the gas mixture multiplied by the absolute system pressure. So, if component number 1 in the mixture is oxygen present at a mole fraction of 0.2 (20 mole percent), and the system pressure is 150 psia [1034 kPa], then:

$$\begin{aligned} P_1 &= P_T \times \text{Mole Fraction } O_2 \\ &= (0.2)(150) \\ &= 30 \text{ psi [207 kPa]} \end{aligned} \quad (6.2)$$

This can be repeated for each component if the gas composition is known.

Henry's Law

Henry says that the amount of a particular gas dissolved in a liquid is directly proportional to its partial pressure in the gas above the liquid.

$$C = KP \quad (6.3)$$

Where:

C = concentration of the gas in the liquid

K = a constant

P = pressure of the gas above the liquid (the partial pressure if a gas mixture is present)

Therefore, if we are interested in decreasing the amount of a gas dissolved in water, it is necessary to decrease the partial pressure of the gas in contact with the liquid. This can be accomplished by decreasing the total pressure, or by decreasing the concentration of the gas of interest in the gas mixture in contact with the water.

Continuing the example with oxygen, if water were in contact with gas at 150 psia which contained 20 mole percent oxygen, we could decrease the oxygen content of the water by:

- Decreasing P_T to less than 150 psia [1034 kPa]
- Decreasing the concentration of O_2 to less than 20%.

Temperature

The solubility of gases in water decreases as the water gets hotter.

Dissolved Oxygen Removal and Exclusion

The solubility of oxygen in water in equilibrium with air at atmospheric pressure is shown in Figure 6.1 as a function of temperature and salinity.

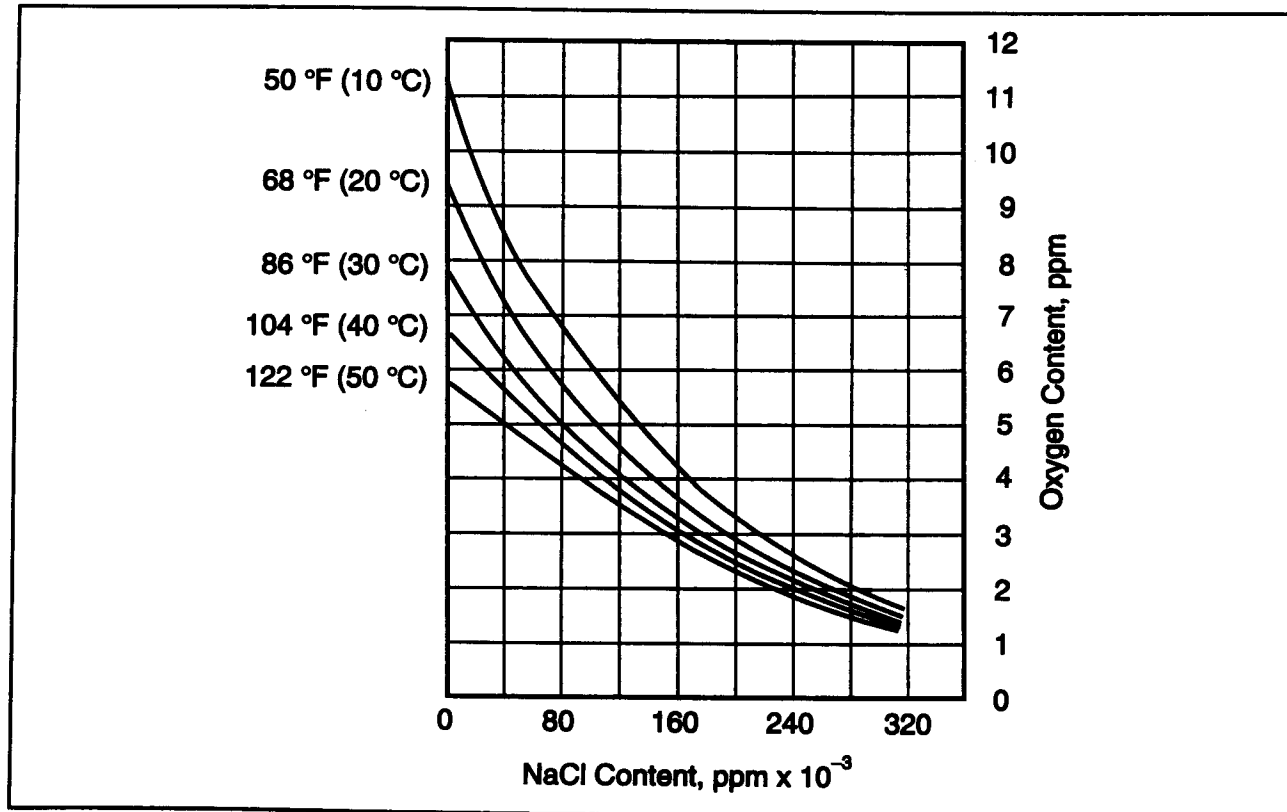


Figure 6.1 Solubility of Oxygen in Water

Mechanical Removal

Heaters

Open heaters or deaerating heaters are used to remove oxygen for some plant operations, but are usually not used in the oilfield. The principle of removal is to: (a) increase the temperature (decreasing oxygen solubility) and (b) put water vapor into the gas space over the water (which decreases the partial pressure of oxygen).

Gas Stripping

Gas stripping is normally performed in counter-current stripping towers containing packing or perforated trays, although tray-type columns are generally preferred because packing is more easily fouled with suspended solids.^(6.1)

The water flows into the top of the tower and the stripping gas is put in at the bottom. (Figure 6.2) It bubbles up through the water, and the trays or packing increase the area of contact between the water and the gas. The rate at which the oxygen comes out of solution increases with contact area.

The amount of dissolved oxygen removed from a given water in a gas stripping tower is a function of several variables:

- Dissolved oxygen concentration in inlet water
- Number of theoretical trays
- Gas/water ratio
- Tower pressure
- Water temperature

These effects are illustrated for seawater in a tray-type column containing 1.5 theoretical trays in Figure 6.3.^(6.2) Note that the efficiency of oxygen removal increases as:

- Tower pressure decreases
- Water temperature increases
- Gas/water ratio increases

It will also increase as the number of trays increases for a given tower design.

A properly designed gas stripping column can reduce the dissolved oxygen content from saturation to 10-20 ppb (0.01-0.02 ppm).

The gas should be free of both oxygen and H_2S . If the CO_2 content of the stripping gas is too high, it will depress the pH of the water and make it more corrosive. In addition, oxygen scavengers don't work very well in low pH waters.

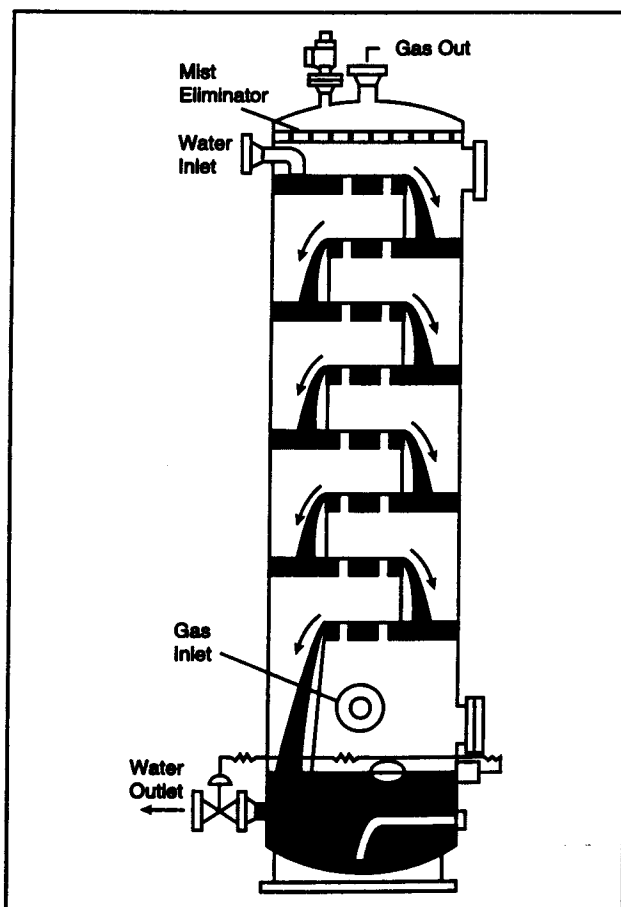


Figure 6.2 Tray-Type Countercurrent Stripping Tower (Courtesy Natco)

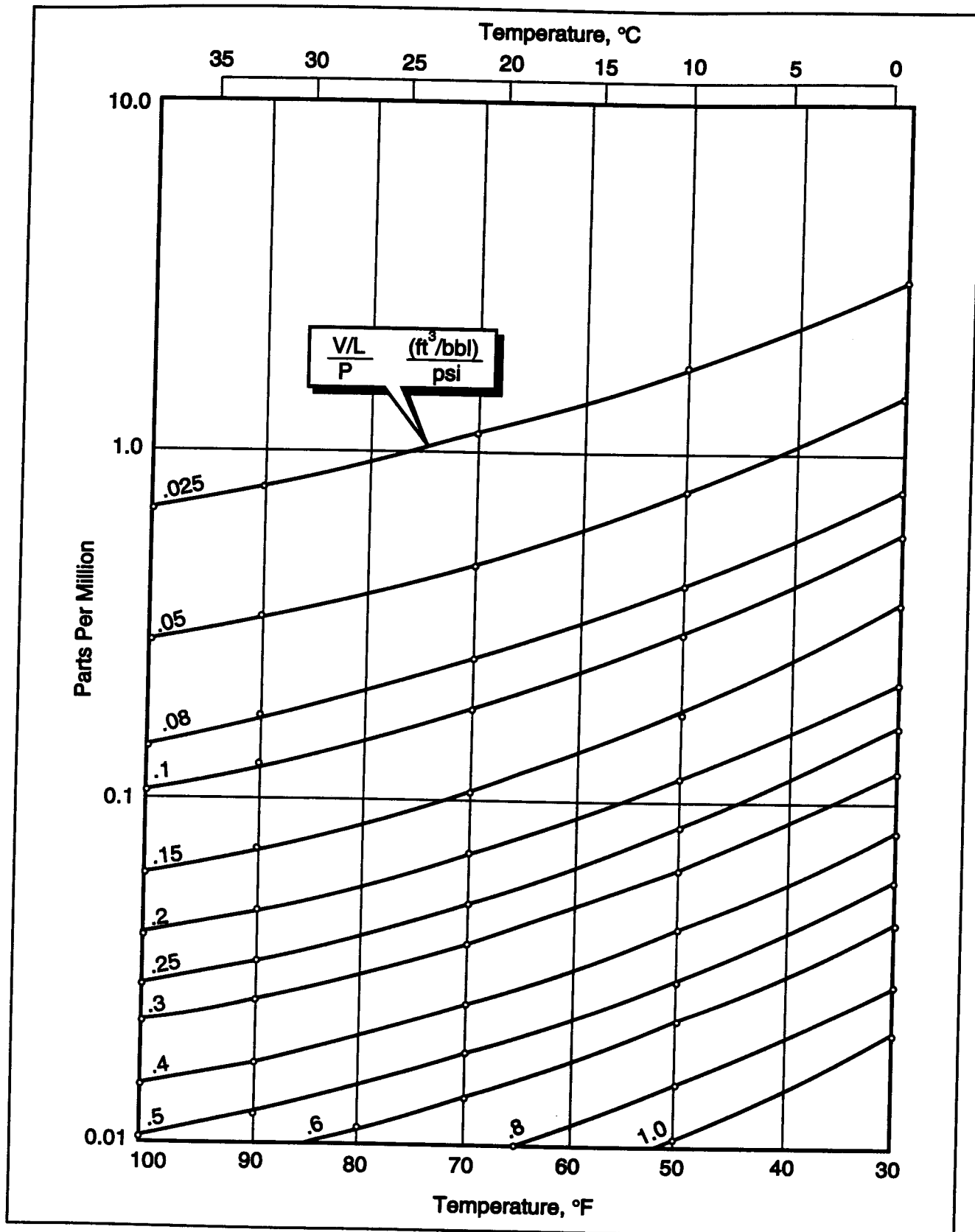


Figure 6.3 Outlet Oxygen Solubility vs Seawater Temperature — Tray-Type Countercurrent Gas Stripping Column^(6.2)

Natural gas is the most common choice for stripping gas, although nitrogen produced by on-site nitrogen plants is used by Aramco to deaerate seawater in Saudi Arabia. Also, Norske Hydro has developed a process in Norway which recycles nitrogen through a novel stripper column utilizing cocurrent flow of the nitrogen and water streams in "serpentine" tubes. Oxygen is removed from the nitrogen after it exits the column by reaction with methanol or methane in a hot catalyst bed before the nitrogen is recycled to the inlet of the stripper.

Where oxygenated water must be artificially lifted, the use of gas lift has been found to remove a large portion of the oxygen.^(6.3) Stripping also can be performed in horizontal pipelines or in flotation cells. However, removal efficiency using these techniques is much lower than in properly designed counter-current stripping towers and they are seldom used.

Design Considerations

Although detailed process design is beyond the scope of this book, there are special considerations that must be considered by the designer.

One factor is the *foaming tendency* of both underground and sea water. In packed towers this foam fills the void spaces and causes *flooding* (liquid flows out the top). This requires that vapor-liquid ratios, and packing types and sizes, should be different than those employed in ordinary hydrocarbon stripping towers.

In trayed columns, tray design must be altered to provide lower than normal gas slot velocities to prevent undue foaming. Downcomers should be designed for low velocity. A tray spacing of less than 20 inches is not recommended ordinarily. Even with optimum design, the overall efficiency is low (theoretical trays/actual trays). Commonly it is in the range of 7-15%. This means that to produce results comparable to those shown in Figure 6.3, a tower with up to about 20 trays might be required. The corresponding height would approach 50 feet [15 m], which limits applications. Tray efficiency depends on the outlet oxygen concentration specified.

Vacuum Deaeration

The principle of vacuum deaeration is to reduce P_T , thereby reducing the partial pressure of oxygen. The pressure is reduced until the water boils. At a temperature of 77°F [25°C], water boils at a pressure of about 0.5 psia [3.5 kPa].

Vacuum deaeration is carried out in a column which contains packing or trays, although packed towers are more common.

The water enters the top of the column through a spray head and flows by gravity down through the packing or trays.

The column will commonly contain 1 to 3 pressure stages. In a packed column each stage consists of a height of packing which is sealed from the stage below by a layer of water in the bottom of the packing. The upper stage operates at the highest pressure. The pressure is progressively lower in each stage as you move down the column. (Figure 6.4)

A practical lower limit of 0.1 ppm dissolved oxygen in the effluent from a single stage tower has been suggested.^(6.4) This limit is imposed by the excessive vacuum pump horsepower required to achieve lower concentrations.

Multi-stage columns are used when very low effluent oxygen concentrations are required. Effluent dissolved oxygen concentrations as low as 10 ppb (0.01 ppm) have been achieved in 3-stage towers.^(6.5)

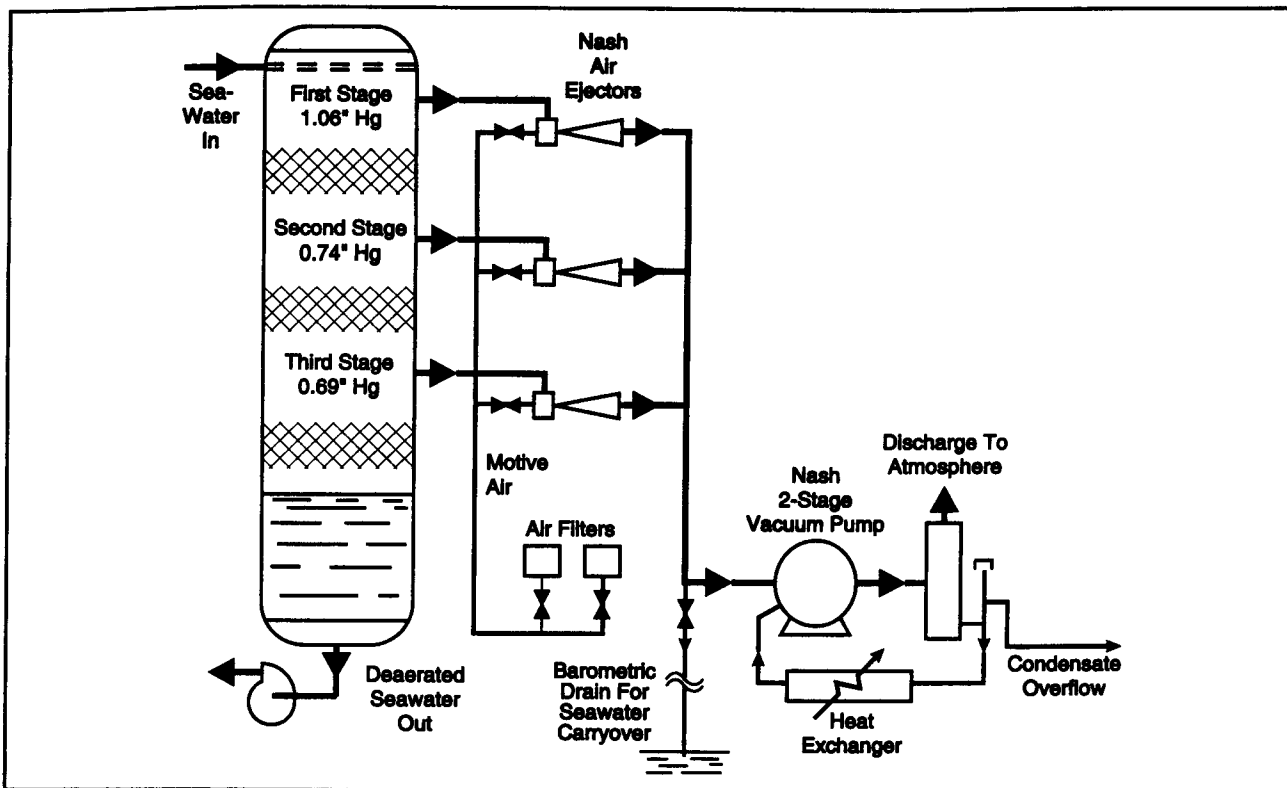


Figure 6.4 Three Stage Vacuum Tower (Courtesy Nash Engineering Co.)

The pressure inside the column is reduced with a vacuum pump. Liquid ring pumps are used in injection water deaerators because of their ability to accept free water carryover from the tower. Water is used as the seal liquid in most installations. A flow diagram of a two-stage liquid ring pump is shown in Figure 6.5.

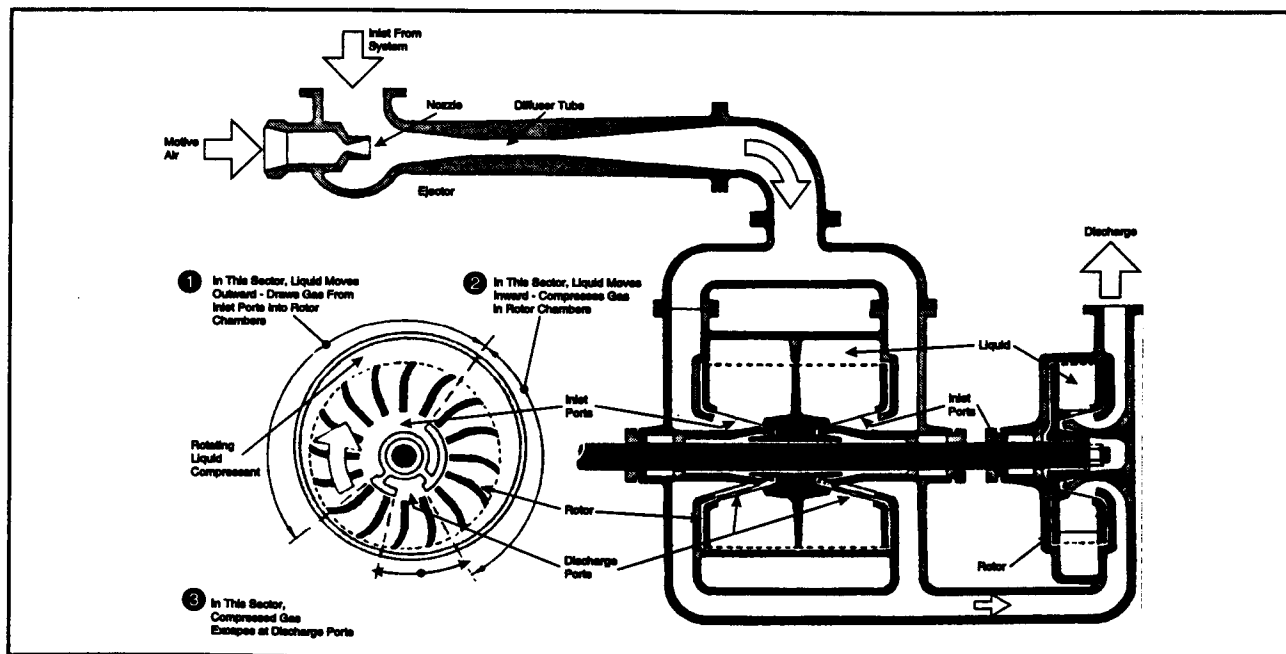


Figure 6.5 Schematic of Two-Stage Vacuum Pump with Air Ejector

The pump shown is equipped with an air ejector, or eductor. Lower pressures can be achieved by the combination of an ejector and a vacuum pump than with the same vacuum pump alone. A schematic representation of the pressure profile across an ejector is shown in Figure 6.6.

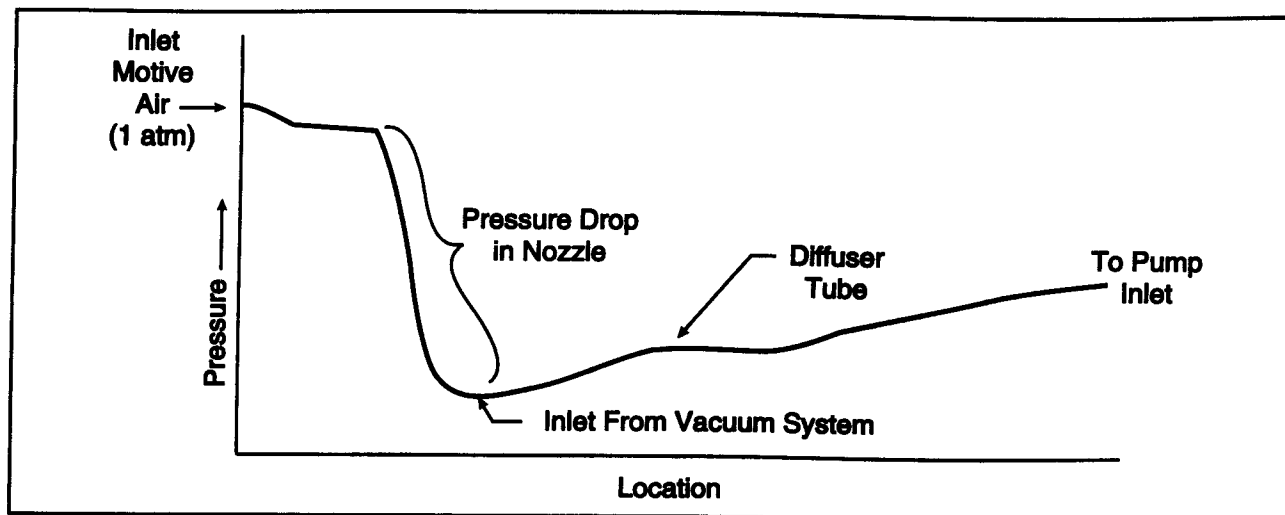


Figure 6.6 Pressure Profile Across an Air Ejector

The use of ejectors has made it possible to operate a multi-stage tower with a single vacuum pump operating separate ejectors for each stage as shown in Figure 6.4.

It is also possible to improve the performance of a vacuum deaerator by the addition of a small amount of stripping gas (usually less than 0.1 ft³/bbl). The presence of the stripping gas provides an additional decrease in the partial pressure of oxygen in the tower, thereby increasing oxygen removal from the water.

Chemical Removal of Dissolved Oxygen

Dissolved oxygen can be removed from water by adding a chemical to the water which will react with the oxygen. These chemicals are referred to as oxygen scavengers.

A summary of oxygen scavenger properties is given in Table 6.1.

TABLE 6.1
Oxygen Scavenger Properties

Compound	Formula	Theoretical Requirement per ppm O ₂	Form	Typical % Active	Requires Catalyst
Sodium Sulfite	Na ₂ SO ₃	7.9 ppm	Powder	100	Yes
Sodium Bisulfite	NaHSO ₃	6.5 ppm	Liquid	35	Yes
Ammonium Bisulfite	NH ₄ HSO ₃	6.2 ppm	Liquid	60	Maybe
Sulfur Dioxide	SO ₂	4.0 ppm	Gas	100	Maybe
Sodium Hydrosulfite	Na ₂ S ₂ O ₄	5.5 ppm	Powder	100	No
Hydrazine	N ₂ H ₄	1.0 ppm	Liquid	35	No

Sulfite Oxygen Scavengers

The most commonly used oxygen scavenger in oilfield operations is the sulfite ion ($\text{SO}_3^{=}$). It is available in a number of forms.

Sodium Sulfite



Theoretically, it requires 7.9 ppm of Na_2SO_3 to react with 1 ppm of O_2 . In practice, an amount in excess of the theoretical requirement is always used. When the oxygen content is near saturation, a ratio of 10:1 (an excess of 25 percent) is common. Removal of small amounts of oxygen (< 1 ppm) usually requires an excess of 2-10 ppm to drive the reaction at an acceptable rate.

Sodium sulfite is purchased as a powder and must be mixed on-site with fresh water prior to injection into the system. A saturated solution of sodium sulfite contains approximately 12 wt% Na_2SO_3 at 0°C .

Sodium sulfite ordinarily reacts very slowly with oxygen at normal operating temperatures, so a catalyst is usually required. (A catalyst is a material which causes a reaction to speed up without directly entering into the reaction.)

Cobaltous ions (Co^{++}) are the most commonly used catalyst. Normally, 0.1 mg/L of cobaltous ion is adequate.

Sodium sulfite may be purchased with the catalyst already added, or cobaltous sulfate hexahydrate (or cobaltous chloride) may be purchased and fed separately into the system. Catalyzed sodium sulfite solutions should be gas-blanketed to prevent reaction with atmospheric oxygen.

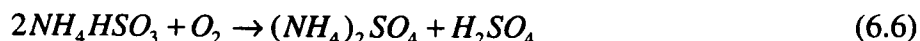
Sodium Bisulfite



Theoretically, 6.5 ppm of NaHSO_3 are needed to react with 1 ppm O_2 .

Sodium bisulfite is normally supplied in liquid form. It must usually be catalyzed just as in the case of sodium sulfite. In addition, because of the acidic nature of the solution ($\text{pH} = 3.5 - 4.0$), the tank must be internally coated or constructed of a corrosion resistant material to prevent corrosion. It is relatively unreactive with atmospheric oxygen due to the extremely low pH of the solution and normally does not require a gas blanket. A saturated solution of sodium bisulfite contains approximately 33 wt% NaHSO_3 at 0°C .

Ammonium Bisulfite



Marketed under several trade names, 6.2 ppm of ammonium bisulfite are theoretically required to react with 1 ppm oxygen. Its primary advantages are threefold:

- Ammonium bisulfite does not react with air because of its low pH and can be stored in open containers.
- Ammonium bisulfite normally does not require a catalyst, although it can be catalyzed if necessary.
- It is more concentrated than other liquid sulfite scavengers. A saturated solution of ammonium bisulfite contains approximately 60 wt% NH_4HSO_3 at 0°C .

This chemical is supplied as a solution with a pH of 4.0-5.0. Therefore, it must be stored in a corrosion resistant vessel. Type 304 stainless steel is commonly used.

Sulfur Dioxide



This reaction requires 4 ppm SO_2 for each ppm oxygen. In most cases, the reaction must be catalyzed with something like Co^{++} ions, just like sodium sulfite. However, in some waters SO_2 will react with oxygen very quickly without a catalyst.

Sulfur dioxide is applied to the system as a gas, is cheaper than sodium sulfite, and less is required. It is not used as frequently as sodium sulfite because it is not as convenient to handle and the catalyst must be added separately. However, it is often used where large quantities of scavenger are needed.

One word of caution: Excessive amounts of SO_2 can lower the pH of the water sufficiently to cause severe corrosion problems.

Factors Affecting Sulfite Reaction Rates

pH

This is the most important variable affecting the rate of the sulfite-oxygen reaction.^(6.6)

When any of the sulfite oxygen scavengers (sodium sulfite, sodium bisulfite, ammonium bisulfite, or sulfur dioxide) are dissolved in water, they will ionize to produce varying amounts of SO_2 , HSO_3^- , and SO_3^{--} depending on the pH of the solution (Figure 6.7). Since only SO_3^{--} reacts with oxygen, pH is very important as it dictates the percentage of the product available to react.^(6.6)

At pH values below 4.5, the sulfite scavengers will not react with oxygen. Reaction rates are not appreciable until pH values exceed 6.0. Further increases in reaction rate occur with pH up to a maximum in the 8.5-10.0 pH range, with a rapid decrease in rate above pH 10.5.^(6.7)

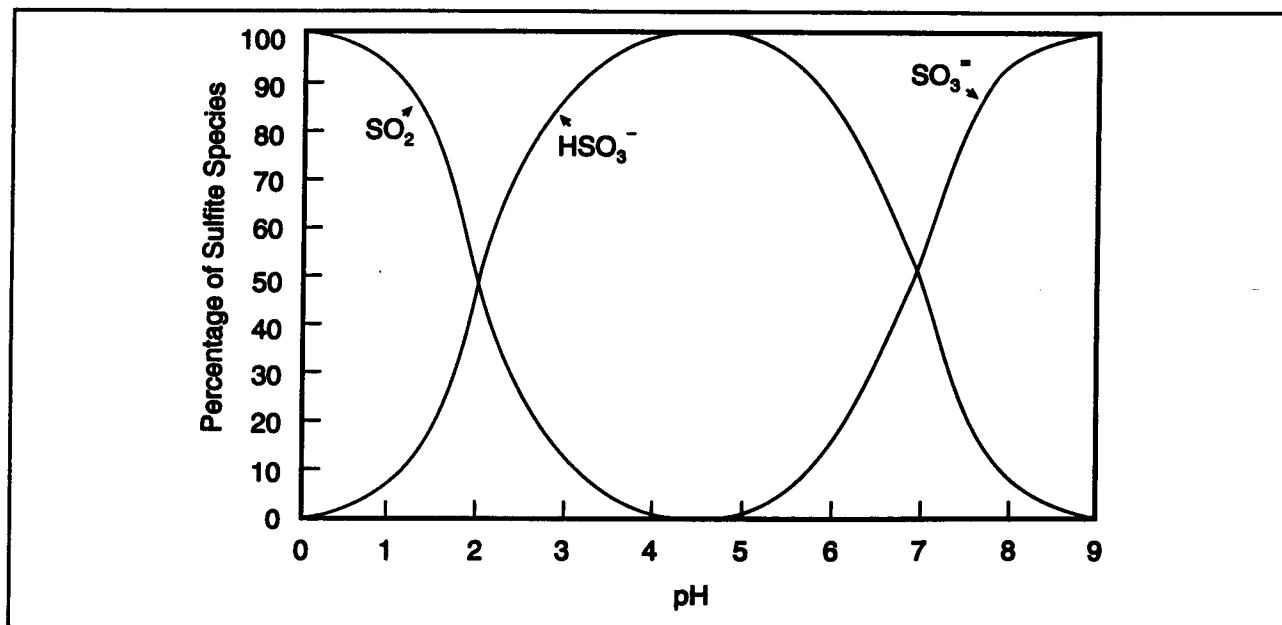


Figure 6.7 Distribution of Sulfite Species as a Function of pH

The effectiveness of Co^{++} as a catalyst decreases as the pH of the water decreases.

Temperature

The rate at which scavengers react with oxygen increases as the water gets hotter. As a general rule, an increase in water temperature of 18°F [10°C] doubles the reaction rate.^(6.8)

Calcium Ion

A high calcium ion concentration in the water (usually greater than 4000 mg/L) leads to the precipitation of the sulfite ion as calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot 1/2 \text{H}_2\text{O}$), thus reducing the amount of sulfite available to scavenge oxygen.^(6.8)

Hydrogen Sulfide

In general, sulfite oxygen scavengers will not be effective if there is more than 5 ppm H_2S present in the water. This is due to the fact that H_2S can reduce the concentration of natural or added catalysts by precipitating them as sulfides. In addition, they can interfere with the basic sulfite-oxygen reaction.

Both sodium sulfite and sodium bisulfite are catalyzed by the addition of cobaltous ions. Unfortunately, the solubility of cobaltous ion is extremely low. If the water contains 0.1 ppm H_2S , the solubility of Co^{++} is only 0.0023 ppb.^(6.6)

If only trace amounts of H_2S are present, it is possible to compensate by increasing the catalyst concentration sufficiently to react with the H_2S and still have some left over to catalyze the scavenger reaction. For example, 0.25 ppm H_2S will precipitate approximately 0.4 ppm cobaltous ion. This means that about 0.5 ppm Co^{++} would have to be added to a water containing 0.25 ppm H_2S in order to have 0.1 ppm Co^{++} left over to catalyze the oxygen scavenging reaction. This approach is not economically feasible in systems containing any appreciable quantity of H_2S because of the high cost of cobalt catalysts.

Treating Chemicals

Both inorganic and organic treating chemicals can adversely affect the reaction rate between sulfite scavengers and oxygen. Some of the known offenders:

1. Chlorine

Oxygen scavengers will react with chlorine, which is a commonly used biocide. When possible, chlorine should be added downstream from the point of scavenger injection. The distance between the scavenger and chlorine injection points should be sufficient to allow the scavenger-oxygen reaction to reach completion before arriving at the chlorine injection point.

If chlorine is injected upstream of the scavenger, additional scavenger must be added to provide sufficient chemical to react with the chlorine plus the amount required to react with any oxygen present.

2. Chelating Agents

Chelants such as EDTA can complex catalysts such as Co^{++} , thus nullifying their effectiveness.^(6.9)

3. Biocides

Aldehydes, which are commonly used as biocides, react with sulfite scavengers to give an insoluble product.^(6.6) Quaternary ammonium chloride will reduce the oxygen scavenging rate by about half.^(6.10)

4. Scale Inhibitors

Commercial phosphonate scale inhibitors drastically reduce scavenging rates. However, phosphate esters appear to have little effect at normal use concentrations.^(6.10)

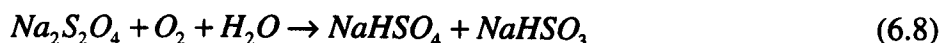
Most corrosion inhibitors, biocides, and scale inhibitors are complex mixtures, and their effect on scavenger reaction rates varies greatly. However, any of these chemicals *can* interfere and should be selected with care. If possible, they should be added downstream of the scavenger.

Other Oxygen Scavengers

Two other oxygen scavengers, sodium hydrosulfite and hydrazine, are used for special applications.

Sodium Hydrosulfite

Also known as *sodium dithionate*, the scavenging reaction is:



The theoretical requirement is 5.5 ppm $\text{Na}_2\text{S}_2\text{O}_4$ per ppm of oxygen. It does not require a catalyst and it can be used in sour systems.

This product is a powder that is much more active than sodium sulfite or bisulfite. It decomposes rapidly in water, so it must be used within a few minutes of the time it is dissolved in water. Because of this, it is seldom used in ordinary water floods.

The primary application of sodium hydrosulfite is in polymer floods. In addition to being an oxygen scavenger, it is capable of reducing ferric iron to ferrous iron, unlike the other sulfite scavengers. The result is that it resolubilizes insoluble ferric hydroxide which may already have formed as a result of earlier contact by the injection water with oxygen.

The formation of ferric hydroxide in polymer floods is extremely undesirable, as the combination of polymer and ferric hydroxide usually results in rapid plugging of the injection wells.

Hydrazine



The hydrazine-oxygen reaction is very slow at normal operating temperatures and is not used in water injection operations. Its primary use is in high pressure boilers, since the reaction proceeds rapidly above 200°F [93°C].

The hydrazine-oxygen reaction cannot be effectively catalyzed at lower temperatures and it is extremely hazardous to handle.

Oxygen Exclusion

Both H_2S and CO_2 are naturally present in many produced waters and we must live with that fact. However, unless you are dealing with a surface water or shallow aquifer water which naturally contain dissolved oxygen, oxygen entry into a system is a man-made event. It may be a conscious decision or an oversight. The net result of oxygen entry is nearly always bad unless appropriate steps are taken,

and it is usually more economical to exclude oxygen from the system. This is often a difficult challenge, since concentrations in the parts-per-billion range have been shown to be damaging.

Gas Blankets — Water Storage Tanks

All tanks handling air-free water should be blanketed with an oxygen-free gas, such as natural gas or nitrogen. A positive pressure of 1-2 ounces [0.5-1.0 kPa] is common. The regulator must be adequately sized to supply gas at the maximum drawdown rate in the vessel. A pressure/vacuum relief valve also must be provided.

Oil blankets should not be used. Oxygen is much more soluble in oil than in water and will rapidly diffuse through an oil layer. At best, an oil blanket will only slow down oxygen entry. It will not prevent entry. It may even create problems since bacteria often thrive at oil-water interfaces.

TABLE 6.2
Dissolved Oxygen Uptake of Water Under Kerosene

Dissolved Oxygen Content of Water (ppm)	Time (min)
1.2	10
2.5	20
4.0	40
7.0	80
8.0	100

In addition to being an ineffective barrier to oxygen, an oil blanket can also create new problems:

- The blanket may be inadvertently pumped into the system, thereby contributing to well plugging.
- The oil can coat suspended solids in the water, making them more efficient plugging agents.
- An oil blanket can encourage bacterial growth since certain types of bacteria often thrive at an oil-water interface.

Gas Blankets — Wells

Both supply wells and producing wells may need to be gas blanketed to prevent oxygen entry. One of the favorite places for oxygen entry is around or through the power cable to a downhole electric pump.

In both supply and producing wells, oxygen occurs most readily when the well is started up after being shut in. A fluid level usually builds in the annulus during shut-in, and when the well is started up, the fluid level is pulled down, sucking in oxygen.

Pumps

Oxygen often enters injection through pump suctions, especially where a net positive suction head is not maintained.

Another source of oxygen entry in centrifugal pumps is leaking seals. If the seals start leaking, air is sucked into the pump. Figure 6.8 is a reproduction of a chart from a recording oxygen meter showing the oxygen concentration downstream of two centrifugal pumps in the same system. The seals in pump No. 1 were leaking, allowing oxygen entry.

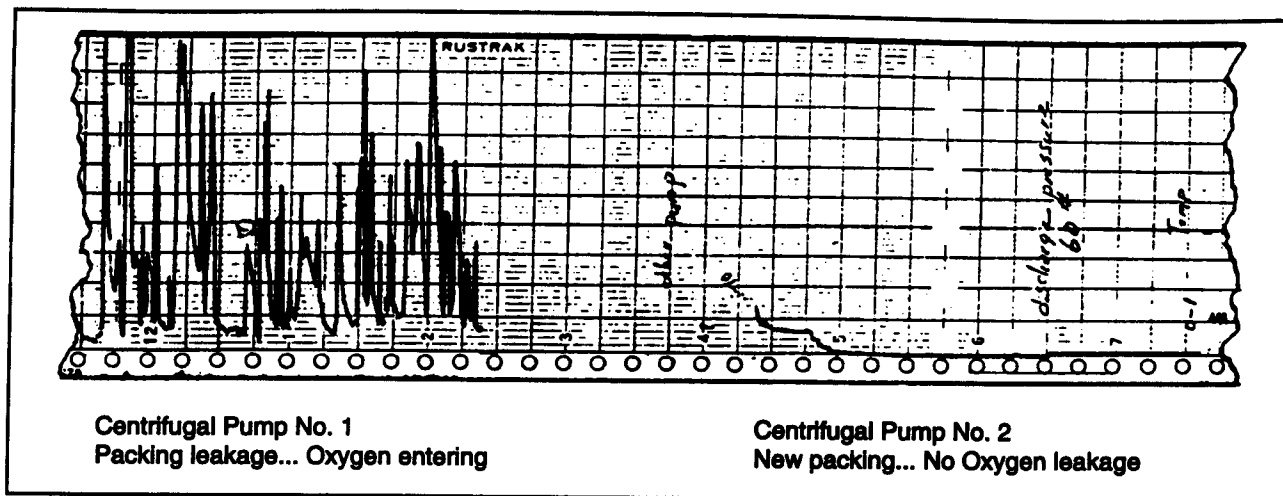


Figure 6.8 Oxygen Meter Recording Chart Showing Oxygen Entry Through Leaking Pump Seals (Full Scale = 0.79 mg/L Dissolved Oxygen)^(6.11)

It is recommended that all centrifugal pumps handling air-free water be equipped with pressurized suction seals. Water from the pump discharge (or other air-free pressurized water) should be piped to the seals.

Valve Stems and Connections

It should be realized that oxygen can travel through water upstream and against a pressure drop due to diffusion. This is one of the things which makes it so difficult to handle. All valve stems and connections such as flanges are likely points for air entry. They must be maintained leak-free.

Monitoring Dissolved Oxygen

Scavengers

It has often been assumed that the catalyzed sulfite-oxygen reaction was so rapid that it would go to completion in a minute or so. Therefore, all that was necessary was to add an excess of sulfite and then make sure that there was a residual concentration of sulfite in the water.

Studies have shown that this approach can lead to serious errors, since many natural waters apparently contain species which interfere with the reaction.^(6.12)

The only safe way to determine how effectively you are doing the job is to measure the oxygen content of the water at the point of interest. This can be especially critical when attempting to determine how far upstream to inject the oxygen scavenger, or how much catalyst to use.

Exclusion

Similarly, only good oxygen measurements taken through a system can tell you whether or not oxygen is being successfully excluded. Because of the fact that oxygen entry is often cyclic, it is

highly desirable to use a recording oxygen meter if oxygen entry is suspected but cannot be pinned down.

Measurement Techniques

CHEMets® have proven to be invaluable for rapid, simple, field determination of dissolved oxygen concentrations in either the ppb or the ppm range. They are highly recommended. (See Chapter 2)

There are several types of dissolved oxygen meters on the market with sufficient sensitivity to measure in the ppb range. Although portable models are available, oxygen meters are used primarily as permanently installed, continuous analyzers in large water treatment plants.

Removal of Hydrogen Sulfide from Water

Mechanical Removal

In order to mechanically remove sulfide from water, it must be in the form of a dissolved gas. You cannot gas-strip an ion. Hence, stripping efficiency improves as the pH decreases.

At pH values less than 5, virtually all of the sulfide dissolved in the water exists as H_2S gas. As the pH rises, more and more of the H_2S ionizes to form HS^- and $S^{=}$. Thus, to maximize the mechanical removal of sulfide, the pH must be lowered sufficiently into the acid range to convert most of it to H_2S . (Table 6.3)

TABLE 6.3
Percentage of Total Sulfides Present as H_2S vs pH

pH	% Total Sulfides Available for Stripping as H_2S
5.0	98
6.0	86
7.0	39
8.0	6
9.0	0.6

Gas Stripping

Gas stripping can be carried out with natural gas, providing the pH of the water can be reduced to a value of 6.0 or lower by upstream addition of acid.

Alternatively, flue gas obtained from submerged combustion or from engine exhausts has been used in several installations.^(6.13) The combustion process should be carefully monitored to be sure that all of the oxygen is being consumed by the combustion reaction.

The flue gas is usually fed into the bottom of a counter-current stripping tower. One of the advantages of using flue gas is that it usually contains about 12% CO_2 which helps to keep the pH of the water down in the range where the bulk of the sulfides are in the form of strippable H_2S .

Aeration

Aeration may be used to remove H_2S from water. This procedure saturates the water with air which often causes as many problems as it solves. There are several types of aerators available.

Although there is some reaction between H_2S and O_2 to form water and free sulfur, the reaction is quite slow, and the primary mechanism of aeration is mechanical stripping.

Chemical Removal of Hydrogen Sulfide from Water

Chemical oxidizers and aldehydes can be used to remove hydrogen sulfide from water. The oxidizers most commonly used in oilfield waters include chlorine, chlorine dioxide, and hydrogen peroxide. The aldehydes used are acrolein and formaldehyde.

In addition to scavenging hydrogen sulfide, all of these chemicals are used as biocides.

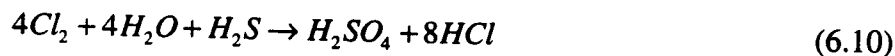
Chemical Oxidizers

Although they are excellent hydrogen sulfide scavengers in acidic and neutral waters, chemical oxidizers can be extremely corrosive to steel if used in sufficient quantities. Also, colloidal sulfur is often the end product of the hydrogen sulfide-oxidizer reaction, which in itself is quite corrosive.^(6.14) In addition, there are many other species present in most waters which will react with oxidizers, making the actual amount required considerably higher than the theoretical amount.

Because of these factors, the use of oxidizers as hydrogen sulfide scavengers is normally limited to the removal of a few ppm of H_2S .

Chlorine

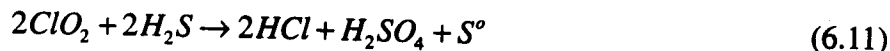
Chlorine may be used to react with small amounts of H_2S .



Theoretically, it requires 8.5 ppm of chlorine to react with each ppm of H_2S .

Chlorine Dioxide

Chlorine dioxide (ClO_2) is used as a bactericide in industrial waters.^(6.15) It can also be used to remove small amounts of hydrogen sulfide from water.



The theoretical requirement is 2 ppm ClO_2 per ppm H_2S .

Hydrogen Peroxide

Hydrogen sulfide can also be removed by reaction with hydrogen peroxide. Under acidic or neutral pH conditions, the reaction proceeds rapidly in the presence of a catalyst, such as iron, to form free sulfur:



The theoretical requirement is 1.0 ppm of peroxide per ppm of dissolved sulfide.

Although there has been concern about the potential corrosivity of hydrogen peroxide, data has been published which indicates this is not a serious problem as long as the treating ratio of $H_2O_2:H_2S$ does not exceed 1.5:1.^(6.16)

Aldehydes

Acrolein

Acrolein ($\text{CH}_2 = \text{CH} - \text{CHO}$) is a powerful biocide as well as hydrogen sulfide scavenger.

The reaction product of the hydrogen sulfide-aldehyde reaction is not known with certainty. However, it is known that higher percentage removals of hydrogen sulfide are achieved as the acrolein/ H_2S ratio is increased. Typically, 4 to 6 ppm of acrolein are used to scavenge 1 ppm of H_2S .

Scavenging ability is maximized in waters having a pH of 6 to 8, a total dissolved solids content of less than 10 000 ppm, and temperatures less than 149°F [65°C]. The reaction requires anywhere from 2 to 20 minutes in most systems.^(6.14)

Acrolein is incompatible with oxygen scavengers, and many corrosion inhibitors and scale inhibitors.

Formaldehyde

Formaldehyde (CH_2O) will also react with hydrogen sulfide. However, the removal efficiency is typically much less than acrolein, as shown in Table 6.4.

TABLE 6.4
Comparison of Sulfide Removal Efficiencies^(6.14)

Chemical Reagent	pH 6	pH 7	pH 8	ASTM Brine
Acrolein	99	99	99	99
Chlorine Dioxide	>99	>99	68	99
Formaldehyde	20	55	43	60
Hydrogen Peroxide	99	94	99	87
Sodium Hypochlorite	>99	99	96	99

Table 6.4 presents a comparison of the hydrogen sulfide scavenging efficiency of the previously discussed chemical reagents. The data shown were obtained using a 3:1 molar ratio (reagent to sulfide) beginning with 100 ppm of hydrogen sulfide. The removal percentages shown were measured after 10 minutes of reaction in phosphate buffers and ASTM brine.

Removal of Carbon Dioxide from Water

The amount of CO_2 which can be stripped from water depends upon water pH just as in the case of H_2S , since the $\text{CO}_2 - \text{HCO}_3^- - \text{CO}_3^{=}$ equilibrium is highly pH dependent.

Aeration

Aeration may also be used to remove CO_2 . As CO_2 is removed, the pH rises, and carbonate scale can form. Also, the introduction of air into the water increases its corrosivity.

Vacuum Degasification

This process has been used to remove CO_2 from water. It can be used indirectly for scale control by lowering the pH to 4 or 5 (thus converting all bicarbonates to CO_2) and then vacuum stripping.^(6.17)

TABLE 6.5
% CO₂ Available for Removal vs pH

pH	% Total Carbonates Available for Stripping as CO ₂
4.0	100
5.0	95
6.0	70
7.0	20
8.0	1

The pH must then be neutralized. This approach has the advantage that it also removes dissolved H₂S and any dissolved oxygen.

FILTRATION

Filtration is the primary method employed to clarify water in oilfield operations. Although sedimentation is used to separate suspended particulates from water in many industries, it will not be discussed here.

Major filtration installations employ backwashable media filters. It should be emphasized that the successful operation of this type of filter requires two steps:

1. Filtration. The suspended solids must be removed from the *water*.
2. Backwash. The suspended solids must be removed from the *filter*.

Failure to successfully accomplish either will result in failure. Successful backwash can be particularly problematic when filtering oily produced water.

Conventional Graded Bed Filters

Different sizes of filter media are placed in a vessel in layers. The largest particles of filter media compose the bottom layer, and successive layers are made up of successively finer particles.

Water flows downward through the finest media layer first. A filter cake is formed in the first few inches of the upper portion of the top layer (finest media) and all of the filtration takes place in the filter cake. The lower layers are simply support beds. (Figure 6.9)

The filter media most commonly used are sand, anthracite coal (anthrafil) and carbon (graphite).

The filter is operated until the pressure drop across the filter reaches about 3.5 psia [25 kPa]. The filter is then backwashed at a high rate to remove the solids which have been filtered from the water from the filter bed. The solids are retained in the top 2-4 inches [5-10 cm] of the bed.

Some rules of thumb:

- The rated capacity of a filter is usually about 2.5 US gpm/ft² of surface area [6.0 m³/hr/m²].
- Recommended backwash rates are 10 US gpm/ft² [24 m³/hr/m²] for anthrafil and 15 US gpm/ft² [37 m³/hr/m²] for sand. The backwash rate should be sufficient to expand the fine

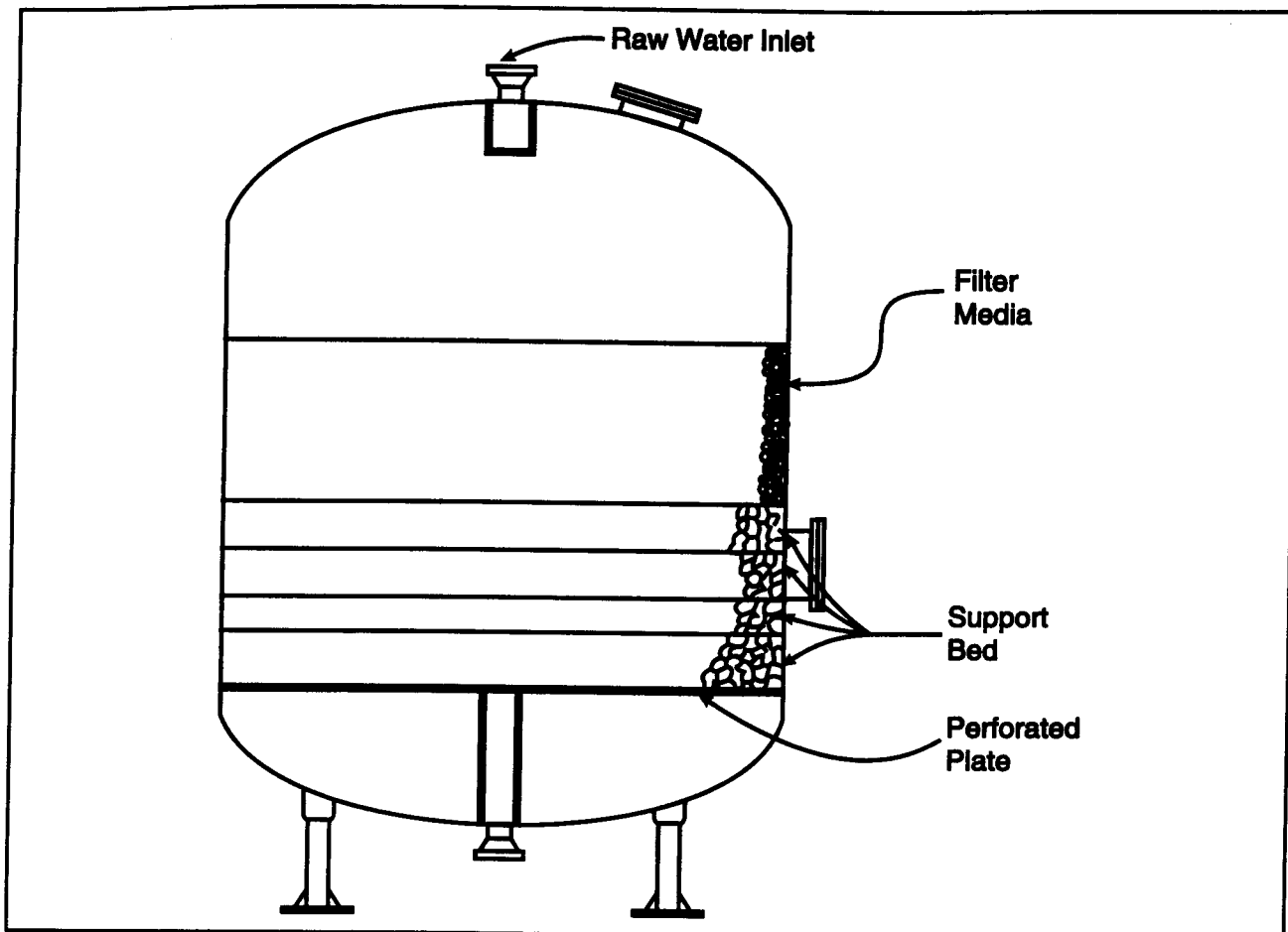


Figure 6.9 Graded Bed Filter (Courtesy Natco)

media by at least 50%. Low backwash rates are not effective. Backwash times are usually 5 to 10 minutes.

- Graded bed filters are capable of removing most particles down to a diameter of 25-50 μm .
- This type of filter is easily fouled by oil carryover.

Conventional graded-bed filters are seldom used in water injection systems because of their inability to remove fine particles.

High Rate Deep-Bed Filters

Deep-bed filters remove suspended particles from water by adsorption on the filter media. No filter cake is formed and the water becomes successively cleaner as it moves through the media. Thus, the whole filter bed takes part in the filtration operation. This is usually referred to as "deep-bed" filtration.

Flow through the filter is in the reverse direction from that normally encountered in conventional graded bed filters. The water flows through the coarse media first and the fine media last.

In most oilfield operations, a polyelectrolyte (an electrically charged polymeric filter aid) is added to the water immediately before it enters the filter. The polyelectrolyte is attracted to both the suspended solids and the filter media and functions as a temporary "glue" to facilitate adsorption of the

dirt particles on the filter media. This capture mechanism makes it possible to remove very small particles from water with an effective polyelectrolyte.

Both upflow and downflow models are available. The choice between downflow filters and upflow filters depends on the characteristics of the solids to be filtered and the desired effluent quality, and can be established reliably only by on-site testing with the water of interest.

Upflow Filters

This term refers to what is basically a graded bed sand filter where the flow is in the reverse direction from that normally encountered in conventional graded bed filters. The water flows upward as shown in Figure 6.10.

The filter bed is held in place by a steel grid structure. The sand builds compression arches beneath the grid members.

The rated capacity of up-flow filters is 6 to 8 US gpm/ft² [15-20 m³/hr/m²], or approximately three times that of a conventional graded bed filter.

“Backwash” takes place in the same direction as filtration (bottom-to-top) and is accomplished with a combination of air and raw, unfiltered water. Air is first blown through the bed to break the compression arches and fluidize or expand the bed. Wash water is introduced while air agitation is still in progress to prevent reforming of the arches during washing. Backwash rates vary from 15 to 20 US gpm/ft² [37-50 m³/hr/m²] for a period of about 10 minutes, followed by approximately 15 minutes to permit the expanded bed to settle. More complex multi-step backwash procedures are also used as illustrated in Figure 6.10.

Particle sizes of 5 to 10 µm can be removed without the use of a *coagulant*. A coagulant such as alum, and/or a *filter aid* (polyelectrolyte), is injected upstream of the filter if fine particles must be filtered from the water. In most cases only polyelectrolyte is required.

Polyelectrolyte concentrations of 0.1 to 2.0 ppm are common. This type of filter has successfully removed particles down to 1 µm in diameter with the help of an effective filter aid.

In summary, the primary advantages of up-flow filters are:

- Appreciably higher flux rates than conventional graded bed filters.
- Enormous flexibility in the size of particles which can be filtered from the water.
- Very high dirt capacity. They are the primary filter used to filter water from Cook Inlet, Alaska, for injection. The suspended solids are primarily fine glacial silt and the concentration is typically around 400 mg/L. Deep-bed upflow filters reduce the suspended solids concentration to 2 mg/L or less with an effective filter aid.
- The ability to handle oil concentrations as high as 500 mg/L in produced waters.

Downflow Filters

In this type of filter the raw water enters the filter at the top and flows downward through a one or two-grade single media bed or a multimedia bed. Both horizontal and vertical models are available.

High rate downflow filters operate at higher flux rates than upflow filters, and often require lower backwash rates. They are capable of removing a wide range of particle sizes.

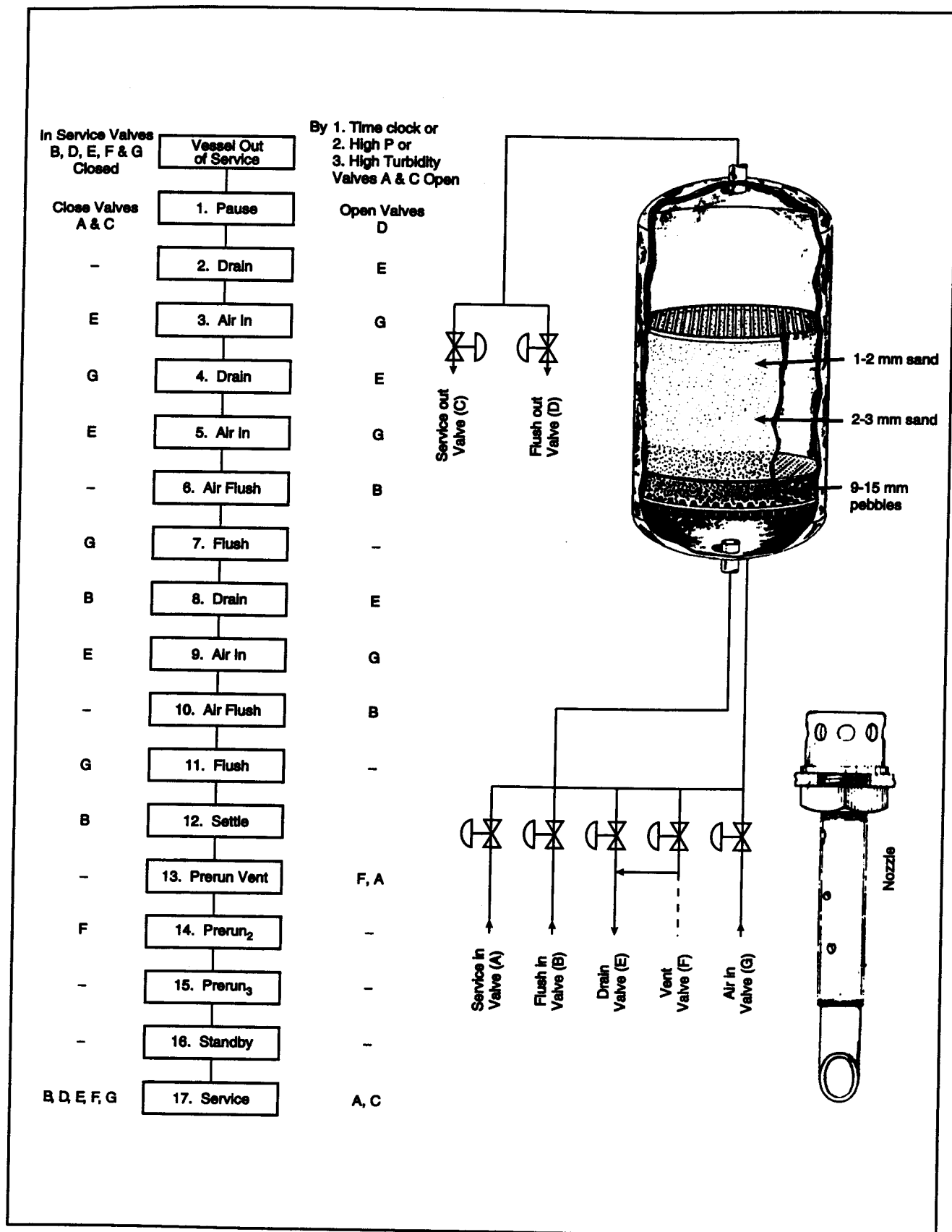


Figure 6.10 L'Eau Claire Deep Bed Upflow Filter (Courtesy US Filter)

Multimedia Filter

The multimedia filter shown in Figure 6.11 uses two types of media: anthracite coal with a specific gravity of 1.5 and garnet with a specific gravity of 4.2. Because of the difference in specific gravities, the lighter anthracite remains on the top of the bed and the finer, denser garnet stays on the bottom. This allows coarse-to-fine filtration just as in the case of the upflow filter.

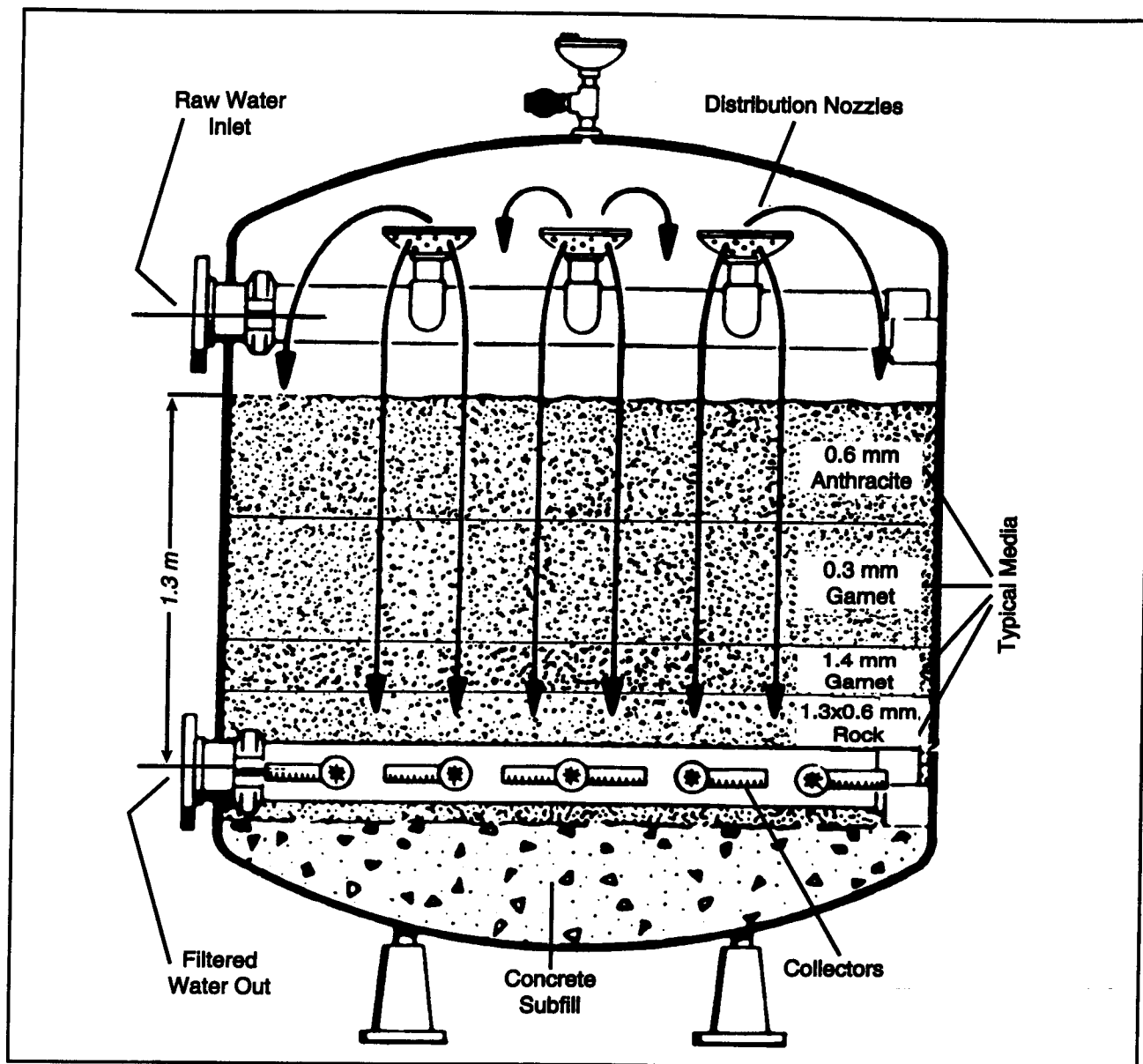


Figure 6.11 Serck-Baker Multimedia High Rate Downflow Filter

As in the case of the up-flow filter, the entire filter bed is utilized. Operational flux rates as high as 15-20 US gpm/ft² [37-50 m³/hr/m²] are quoted, although many units are operated at 10-12 US gpm/ft² [25-30 m³/hr/m²].

Backwash is from bottom to top as in the case of conventional filters. Air is used to expand the bed, followed by backwash with filtered water. Backwash rates of 12-15 US gpm/ft² [30-37 m³/hr/m²] for periods of 7 to 10 minutes are common.

Particle sizes of 7 to 10 μm can be removed without a filter aid. Removal down to 1-2 μm can be achieved with 0.5 to 2.0 ppm filter aid.

This filter should be considered for applications where the suspended solids concentration is 50 mg/L or less. When filtering produced water the oil content should not exceed 30 mg/L.

Nut-Shell Filters

WEMCO Silver Band Filter

This is a deep-bed downflow filter which utilizes a mixture of ground pecan shells and walnut shells as the filter media (Figure 6.12). Although this type of filter can be used to filter any type of water, its primary application in the oilfield is for the removal of suspended solids and oil from produced water.

This kind of filter differs from conventional filters in two ways:

1. The nut-shell media is preferentially water wet. This reduces the tendency of the media to become coated or fouled with oil.
2. The filter is not backwashed in the conventional sense. The fluidization pump located on top of the filter is turned on and the media is fluidized and circulated past the separator screen located in the center of the vessel. (Figure 6.12) Dirty, unfiltered water is then admitted to the vessel while circulation continues. The accumulated solid particles and oils pass through the separator screen and out through the contaminant discharge line. The filter media is retained in the vessel by the screen.

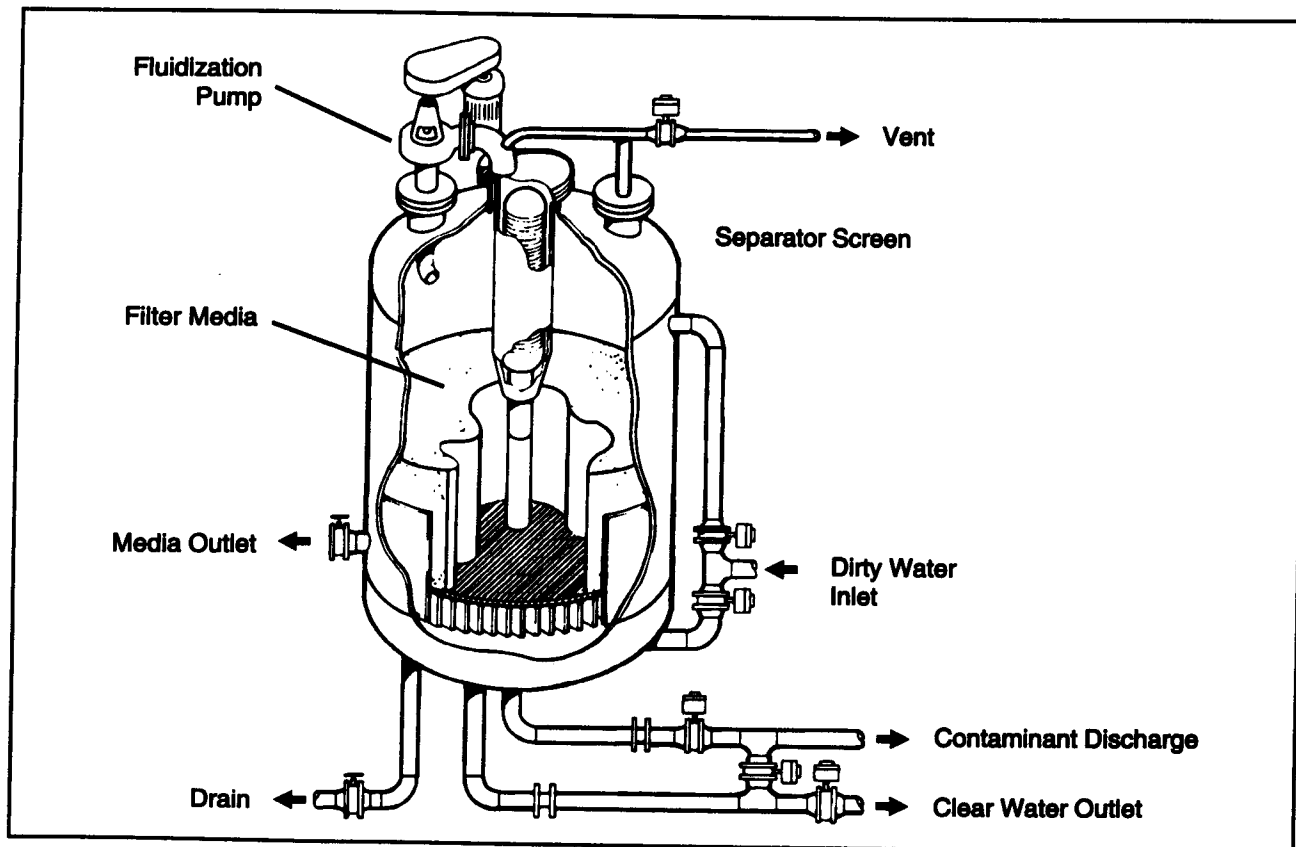


Figure 6.12 WEMCO Silver Band Filter

Regeneration volume is typically less than 1% of throughput and regeneration times are as short as 14 minutes.

The design flux rate of 13.5 to 15.0 US gpm/ft² (33-37 m³/hr/m²). Particle removal efficiency is said to be 98% of all particles larger than 2 µm in most applications. Maximum concentrations of 100 mg/L TSS and 100 mg/L oil are recommended by the manufacturer.

Hydromation Filter

This is a deep-bed downflow filter which is very similar in concept to the Silver Band filter and is primarily used to filter produced water (Figure 6.13).

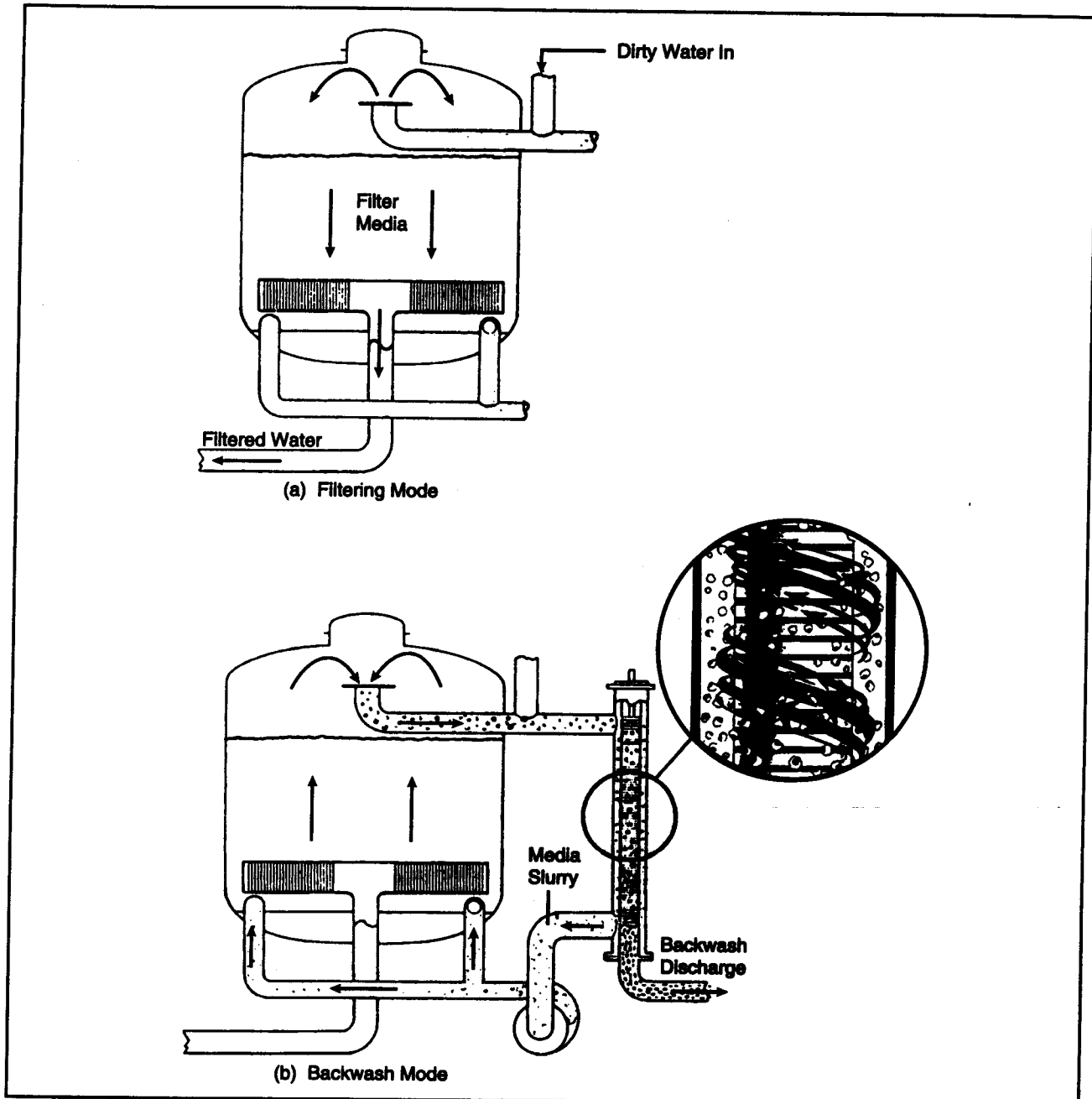


Figure 6.13 Hydromation Walnut-Shell Filter

Conceptually, this filter differs from the Silver Band in two ways:

1. Ground black walnut shells are used as filter media rather than the pecan shell/walnut shell mixture.
2. The bed regeneration technique is the same as for the Silver Band, except that the media is circulated through a scrubber-separator which is located outside the vessel as shown in Figure 6.13. The slots in the dirt-collector tube are large enough for dirt to pass through, but smaller than the size of the media grains, allowing the dirt and oil to be separated from the media into the backwash discharge.

The backwash discharge volume is only about 1% of the total filter throughput.

Design flux rates are typically around 12 USgpm/ft² [29 m³/hr/m²], although operational rates are sometimes higher.

Polyelectrolytes are often used to enhance filtration performance in oil-free waters such as seawater or river water. Polyelectrolytes are not normally used when filtering oily produced water.

Particle removal efficiencies are said to be comparable to those obtained with other deep-bed filters.

Dual Flow Filter

The dual flow filter is basically a combination of an upflow filter and a multimedia downflow filter in the same shell. (Figure 6.14)

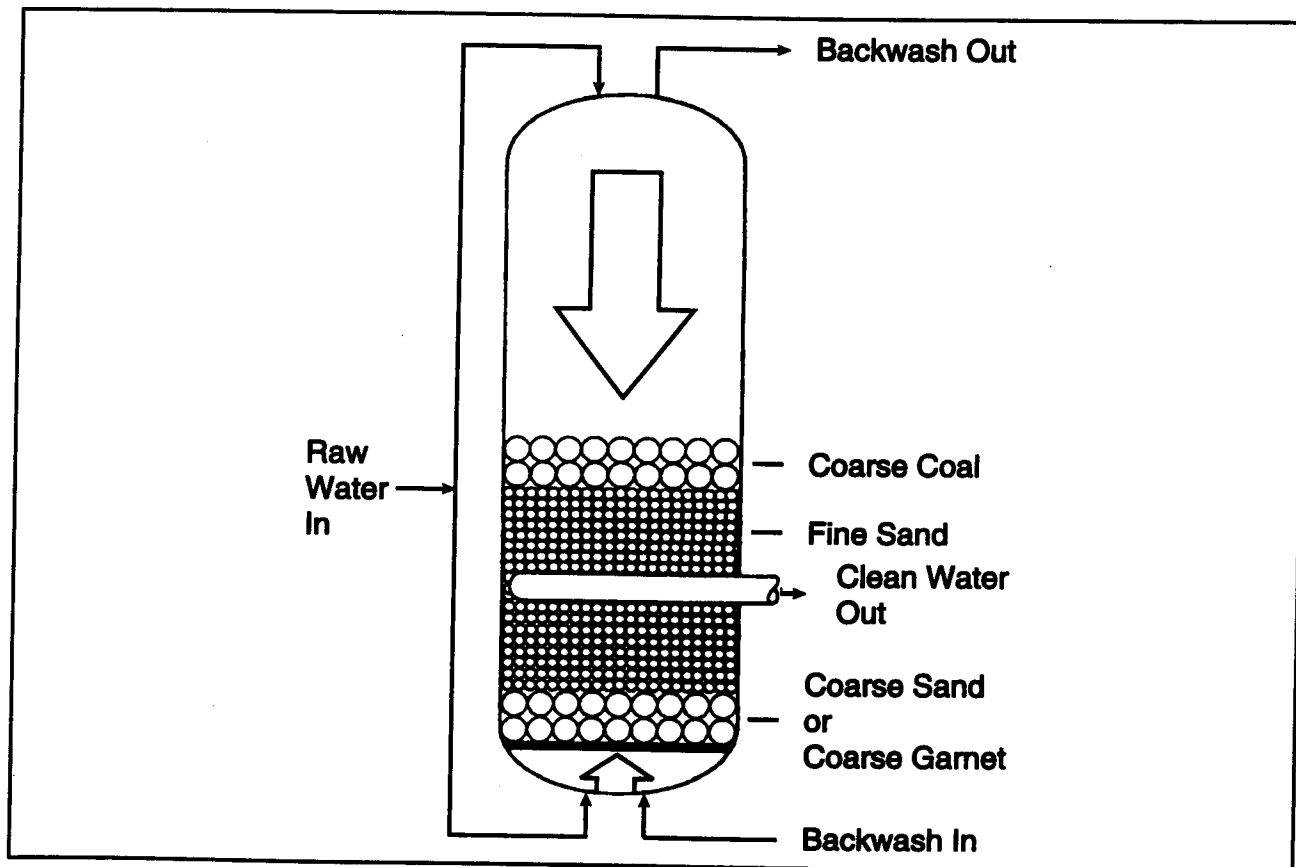


Figure 6.14 Dual Flow Filter (Courtesy Natco)

The filter shown contains three layers of media which are described in Table 6.6.

TABLE 6.6
Filter Media Description

Layer	Material	Specific Gravity	Typical Layer Thickness
Top	Coarse Anthracite	1.5	12 in. [30 cm]
Middle	Fine Sand	2.6	60 in. [150 cm]
Bottom	Coarse Garnet	4.2	12 in. [30 cm]

Half of the raw water enters from the bottom and half enters from the top, with a common outlet in the middle. This results in downflow, coarse-to-fine filtration in the upper half of the filter, and upflow, coarse-to-fine filtration in the lower half of the filter. Thus, it is essentially two filters in the same shell.

This filter is rated at 10-20 US gpm/ft² of filtration surface [25-50 m³/hr/m²]. Since there are two inlet surfaces (top and bottom), the rating becomes 20-40 US gpm/ft² [50-100 m³/hr/m²] of vessel cross section.

Diatomaceous Earth Filters (DE Filters) ✕

Diatomaceous earth (DE or Diatomite) is nearly pure silica formed from fossilized single-celled marine plants. It is mixed into a water slurry and fed into the filter, where it deposits on a supporting screen or cloth. This porous bed or deposit of DE acts as the filter. Some DE must also be added continuously to the water to maintain the porosity of the filter cake. This continuous feed is called "body feed."

The filter is operated until the pressure drop across the filter reaches a maximum of about 35 psi [240 kPa], (depending on the filter). Then the filter is backwashed and both the filter media and the material filtered are discarded.

Some rules of thumb about DE filters:

- DE filters are the most complicated filters to operate of those used in the oilfield.
- They are economically feasible only when the suspended solids do not exceed 30-50 mg/L.
- The "average" DE filter is operated at a rate of 1.0 US gpm/ft² [2.5 m³/hr/m²], with a maximum rating of about 2.0 US gpm/ft² [5.0 m³/hr/m²]. However, overall space requirement is less than for conventional or high-rate filters.
- DE filters will remove entrained oil from water, but this results in rapid fouling of the bed.
- They will remove very fine suspended particles — as small as 0.5 µm in diameter.
- DE can and usually does bleed through the filter and is an excellent formation plugging material. Downstream cartridge filters are strongly recommended to catch any bleed-through.
- Diatomaceous earth must be supplied and constitutes a logistical problem. Also, disposal of the used DE and disposal of the associated filtered solids can prove to be an operational difficulty.

DE filters do a superb job of removing very fine particles and are used in many industries. However, they are almost never used in water injection systems because of the requirement to supply new DE, dispose of used DE, and provide adequate operational supervision.

Cartridge Filters (X)

Cartridge filters are available in a wide variety of materials and pore sizes. Both disposable and back-washable filter cartridges are marketed.

Common materials of construction for the filter elements include:

- Pleated paper, polypropylene, glass fiber
- Sintered metals (Stainless steel, Monel, etc.)
- Woven metal screen mesh
- Woven wool or cellulose fibers
- Epoxy bound sand
- Molded fibers

Some typical disposable filter cartridges are shown in Figure 6.15.

Some cartridges operate on a surface filtration principle, with the formation of a filter cake on the outer cartridge surface. Others utilize true "depth type" filtration, with the penetration of filtered particles well into the fiber body.

Cartridge filters possess a limited solids capacity and have traditionally been used primarily as a precautionary or secondary filter. They are often used at individual wellheads or upstream of meters.

Disposable cartridges are normally used where very infrequent plugging is anticipated. Otherwise, supply, labor and disposal problems can become quite serious.

Backwashable cartridge filters should be considered if it appears likely that frequent filter plugging will occur or if supply and/or disposal of filter cartridges poses a problem. Backwashable cartridge elements can be used in a normal cartridge filter case and be removed for backwash in a special cleaning unit. True backwashable cartridge filter units are also available which automatically backwash the cartridge in-place.

Automatic, backwashable cartridge filters such as the one shown in Figure 6.16 may be considered as a primary filter to provide water of satisfactory quality with minimum investment and space requirements if:

- The unfiltered water has a very low suspended solids content.
- The suspended particle size distribution is compatible with the filtration capability of the filter element.
- The nature of the solids is such that they can be backwashed effectively from the filter. For example, organic materials are normally difficult to backwash.

However, it should be remembered that these units have limited capacity and their use as a primary filter is justified only in very special cases.

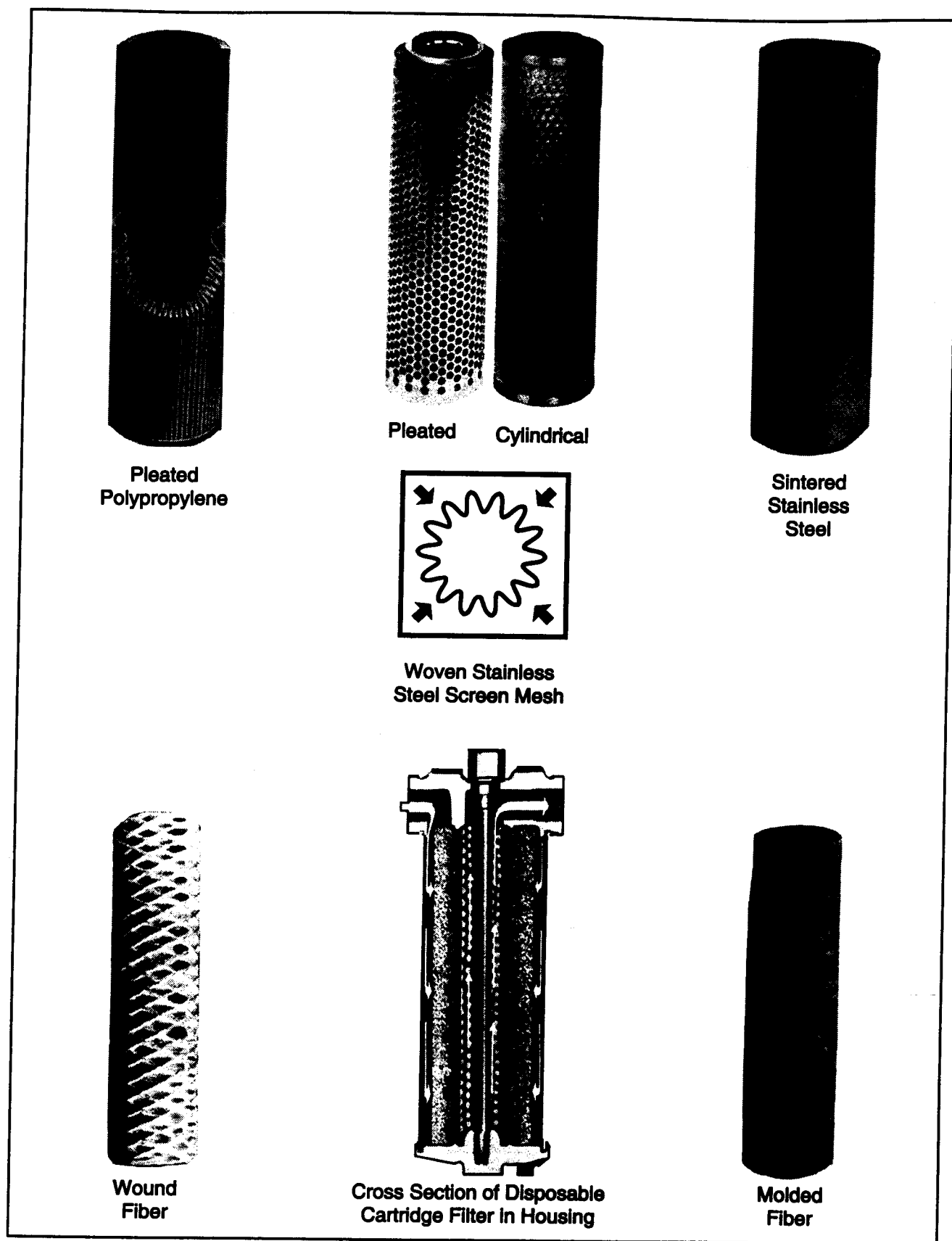


Figure 6.15 Typical Disposable Filter Cartridges

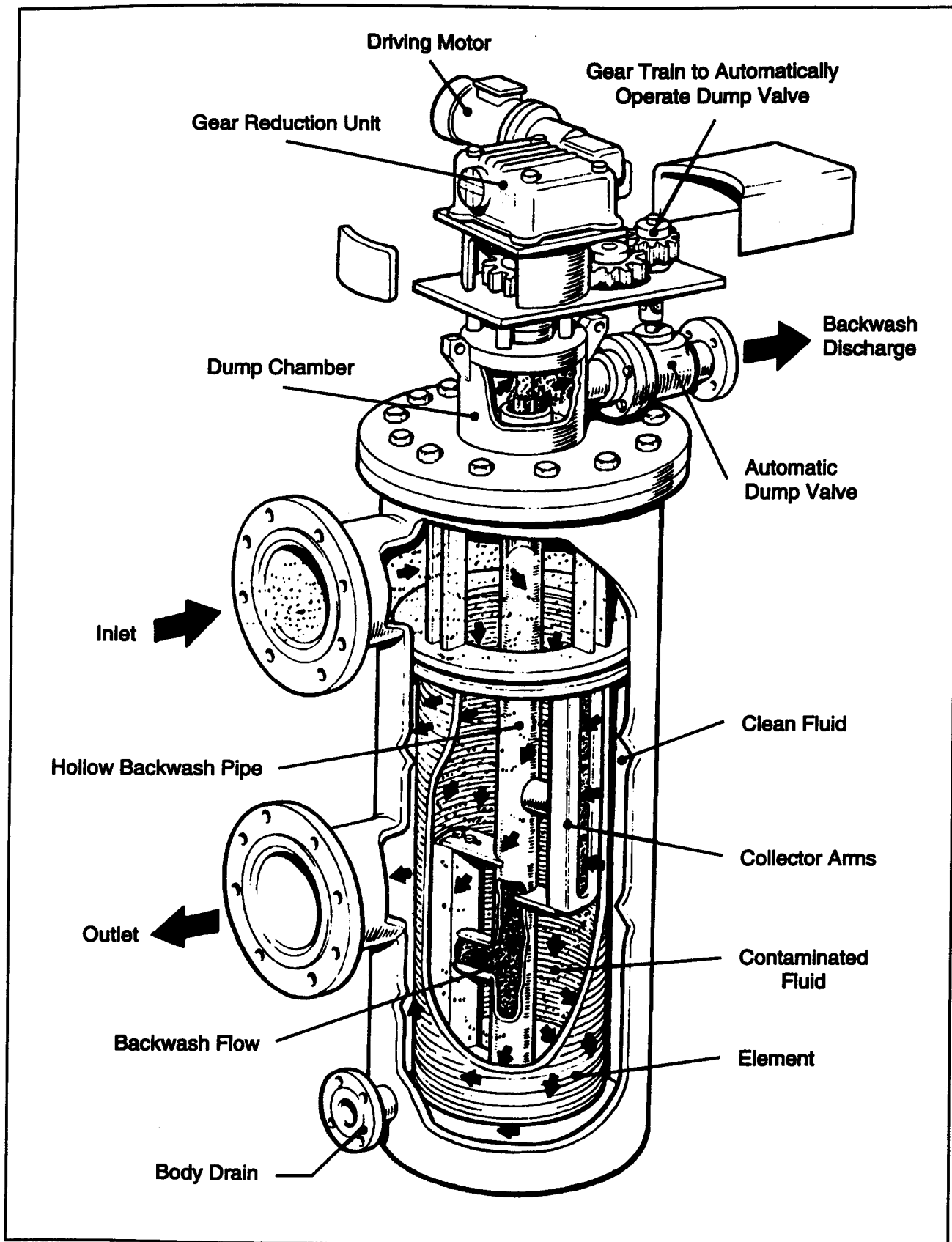


Figure 6.16 Automatic Backflushing Cartridge Filter (Courtesy Plenty and Son Ltd.)

The PuriTech Seawater Filter

This filter was developed in Norway by ABB Environmental for use in the North Sea. Its major advantage is its relatively low weight and space requirement.

The filter utilizes two sets of absolute-rated polypropylene cartridge filters operated in series within a single vessel. The first set, or stage, is made up of cartridges with a relatively large pore size while the second set has a smaller pore size and acts as a polishing filter. Virtually all particles larger than 2 μm can be removed with this unit.^(6.18)

The filters are backwashed with pulsed air and seawater one or more times per day. However, most of the suspended solids in North Sea seawater are marine organisms which are sticky and difficult to remove from cartridge filters with normal backwash procedures. This problem is overcome by re-conditioning the cartridges with a concentrated sulfuric-acid foam approximately once every 9 days.^(6.18) The acid dehydrates the residual organic material in the cartridges and converts it to finely divided carbon. The carbon is non-adherent and is easily washed away.

About 90 minutes is required for acid regeneration of the two-stage filter.

Cartridge Filter Ratings

Cartridge filters are rated according to the size of the particles they can remove from a liquid. Unfortunately, the micron rating of a filter often doesn't mean very much.

Nominal Ratings

Most cartridge filters are assigned a nominal micron rating. However, the nominal rating has no standard definition, and can be very misleading. For example, one can purchase several filters from different manufacturers, each with a nominal rating of 10 μm , and they will probably perform differently. Furthermore, particles larger than 10 μm will be found downstream of the filter. It is not uncommon for a nominal 10 μm cartridge filter to pass particles that range in size from 30 μm to over 100 μm .

Most of the nominal rating test procedures are based on the *weight percent* of the particles of a given diameter which are removed by the filter, rather than the *number* of particles removed. For example, a nominal rating of 10 μm based on 98% removal efficiency means that 98% by weight of all particles 10 μm and larger were removed by the filter, using a specific contaminant at a given concentration and flow rate. If any of the test variables are changed, the results may vary significantly.

Therefore, in addition to the nominal micron rating, it is important to know the removal efficiency at that rating, and the test method used by the manufacturer to determine the rating.

Nominal pore sizes less than 1 μm are available, but pore sizes less than 5 μm are seldom used in oilfield operations.

Absolute Ratings

Some cartridge filters have an absolute rating rather than a nominal rating. A 10 μm absolute rated filter is supposed to remove 100% of all rigid particles 10 μm in diameter or larger.

Filtration Ratios and Filter Efficiency

The Filtration Ratio, or β Ratio, can be used to rate cartridge filter performance and is defined as follows:^(6.19)

$$\beta_x = \frac{U_x}{U_d} \quad (6.13)$$

Where: U_x = Number of particles upstream of filter with a diameter $\geq x$ μm
 U_d = Number of particles downstream of filter with a diameter $\geq x$ μm .

The particle removal efficiency for a particles with a diameter $\geq x$ μm is given as follows:

$$\eta_x = 100 \left[\frac{U_x - U_d}{U_x} \right] = \frac{\beta_x - 1}{\beta_x} \quad (6.14)$$

TABLE 6.7
Beta Value vs % Removal

β_x	% Removal
1	0
2	50
10	90
100	99
1000	99.9
10 000	99.99
100 000	99.999

The Beta rating system can be used to measure and predict filter performance. The relationship between Beta values and percent removal is shown in Table 6.7.

A Beta value of 10 000 is normally used as an operational definition of an absolute rating.

Filter Selection

It is impossible to theoretically predict filter performance. The only rational way to select a filter is to conduct comparative on-site performance testing with small-scale pilot filters and the water of interest.

All filters should be tested simultaneously to ensure that each unit is evaluated under identical conditions. The following variables should be measured as a function of time:

- Particle size distribution upstream and downstream of the filter.
- Suspended solids concentrations upstream and downstream of the filter.
- Pressure drop across the filter versus flow rate.

These measurements will make it possible to evaluate particle size removal efficiency, the dirt capacity of the filter, and filter life.

Backwashable filters should be run through multiple filter-backwash cycles to *ensure that the filter can be effectively backwashed*. The pressure drop across the filter at the beginning of each filter run, immediately after backwash, should remain relatively constant.

Filter Monitoring

Filter performance can be monitored by:

- Turbidity measurements
- Suspended solids content
- Water quality measurements

Normally, turbidity measurements are sufficient for routine performance. However, determination of suspended solids, particle size distributions and/or water quality should be made periodically to actually *measure* filter performance.

SUSPENDED OIL REMOVAL

Oil carryover can cause many problems in a water injection system and should be minimized. The following section briefly describes those oil/water separation technologies most commonly used in oilfield production operations.

The first step in reducing oil carryover is to make sure that the primary oil/water separation process is functioning properly and that the demulsifier is doing its job. Remember that there are two objectives for the demulsifier: clean oil *and* clean water. Run a thorough check to ensure that the treating temperature, residence time and demulsifier selection and concentration are acceptable. If this does not produce water with the desired oil content, one or more oil/water separation processes must be installed.

Skim Tanks

Skim tanks are the simplest and most widely used device for removing dispersed oil from water. They are simply vessels which provide retention time so that free oil will have time to rise to the surface where it can be skimmed off and collected. There are many different designs ranging from field-modified storage tanks to purpose-built vessels incorporating special inlet and outlet systems such as in Figure 6.17. Skim tanks are used primarily to separate the bulk of the free oil from the water and are often used upstream from other oil removal equipment.

Vertical Downflow Skim Tanks

Most water skim tanks in onshore installations utilize a vertical downflow configuration because of its simplicity and low space requirements. In the downflow design, the oil droplets must rise upward countercurrent to the downward flow of the water.

Three commonly used downflow geometries are shown in Figure 6.18. In the first two designs, the emulsion is distributed laterally near the center one-third of the tank by passing through a spreader bar network, or discharging from the inlet line upwards toward a spreader plate. Some coalescence occurs in the zone between the spreader and the water collector, and the buoyancy of the oil droplets causes them to rise counter to the water flow. Oil is collected and skimmed off the surface.

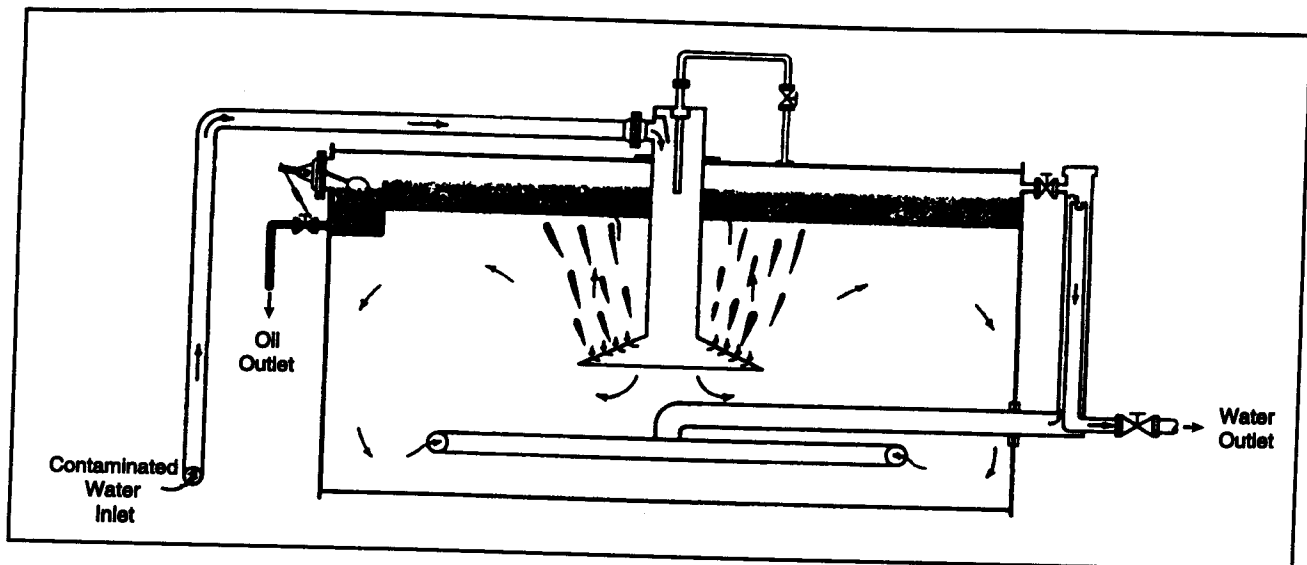


Figure 6.17 Skimmer Tank (Courtesy Natco)

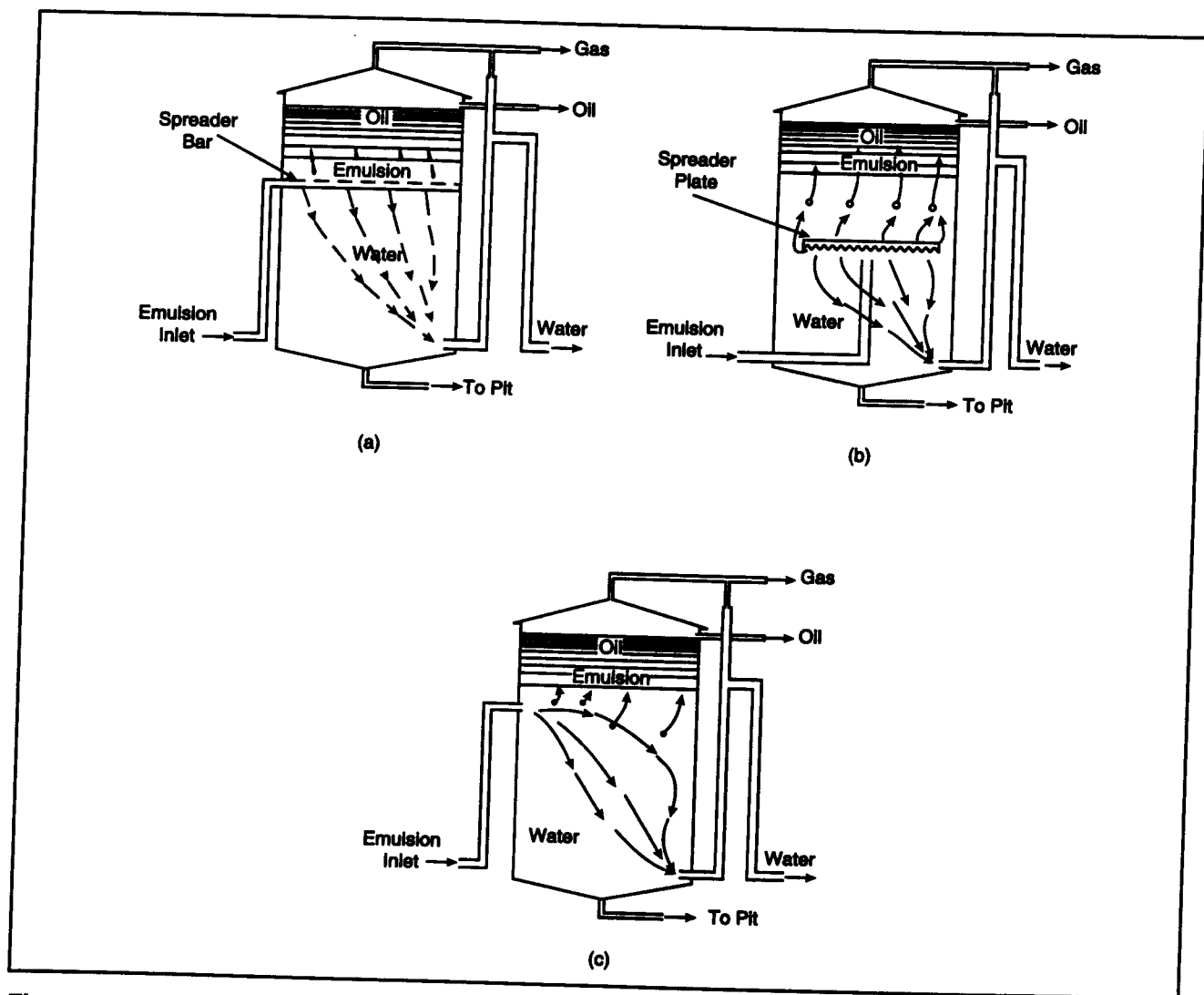


Figure 6.18 Common Skim Tank Designs

The basic disadvantage of these designs is channeling. Only a fraction of the available tank volume is used, and the actual transit time through the vessel is a small percentage of the theoretical value.

Field tests on the designs shown in Figure 6.18a and 6.18b show volumetric utilization efficiencies of 20% or less, while the third design has an efficiency of less than 5%.

Vortex Tank

The vortex tank is an improved vertical downflow skim-tank design developed by Amoco. (Figure 6.19) This design exhibits much better volumetric utilization efficiencies (typically 40-80%) and higher oil recoveries than more conventional configurations. Furthermore, existing vessels can be easily converted to a vortex tank.

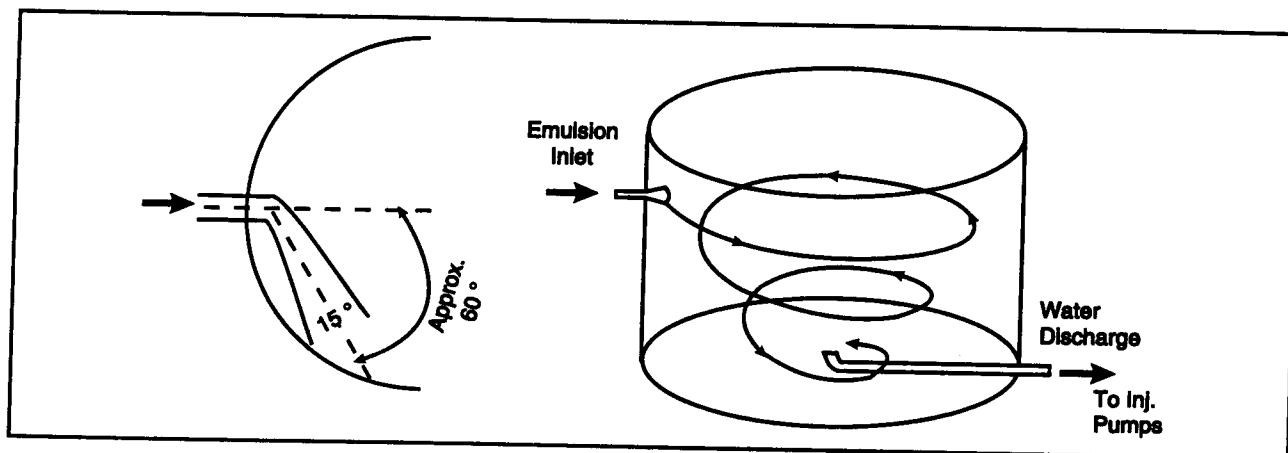


Figure 6.19 Vortex Flow System

The vortex design maintains high recovery efficiency because of its unique flow pattern which helps achieve high volumetric utilization. It is considered to be one of the best overall field-proven skim-tank configurations because of its simplicity, high recovery efficiency, and low space requirements.

The design employs a low velocity vortex current to overcome the tendency of oily water to channel directly from the tank entry to the discharge. The vortex current is created by injecting the water into the settling tank tangential to the tank wall, a short distance below the oil-water interface. The water enters the tank at a 60 angle through a horizontal converging-diverging diffuser nozzle. The nozzle is specially designed to reduce turbulence in the tank near the nozzle exit. The water is discharged near the bottom at the center of the tank.

The incoming fluid causes the fluid in the tank to rotate slowly about the vertical centerline of the tank. This rotational velocity is much too small to result in any separation by centrifugal force; however, it is adequate to overcome any tendency for the incoming fluid to channel directly to the tank outlet before gravity separation of the oil and solids from the water can occur.

Oil rises to the surface where it is continually skimmed by the oil skim line. This fixed line is normally located as high in the tank as possible. It is a common practice to place it one foot down from the top of the tank.

Horizontal Skim Vessels

Many offshore installations use horizontal pressure vessels similar to the one shown in Figure 6.20 as skim tanks. Safety concerns often dictate the use of a pressure vessel due to the possibility of overpressuring and gas venting. In addition, horizontal vessels are typically more efficient than vertical vessels.

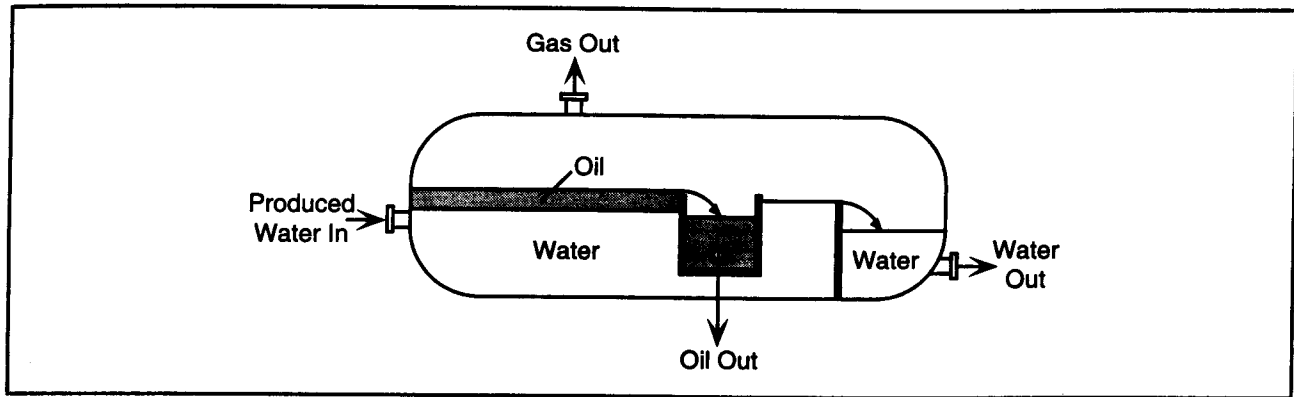


Figure 6.20 Horizontal Skim Vessel (Courtesy ESI)

Flotation Cells

Gas flotation is a process wherein fine gas bubbles are formed in the water which attach themselves to particles of oil or solids and help to lift them to the water surface for collection.^(6.20) Coagulants, polyelectrolytes or demulsifiers may be added to improve performance.

The essential features of a gas flotation unit are:

- Introduction of finely dispersed gas bubbles into the stream to be treated.
- A zone of minimum turbulence.
- A means to remove the floated material from the water surface.

Commercial gas flotation units may be classified by the way in which gas is introduced into the water. There are two basic classifications: dissolved gas flotation and induced gas flotation.

Dissolved Gas Flotation

The gas is dissolved in the water under pressure. When the water flows into the flotation vessel, the pressure is released allowing the gas bubbles to evolve.^(6.20-6.22) (Figure 6.21) These units are seldom used in modern oilfield operations because of their rather ponderous size, high cost and the generally better results achieved with dispersed gas flotation.^(6.21)

Induced Gas Flotation

The gas is mechanically dispersed in the water using either a mechanical rotor or an eductor.

1. Rotor-Type Induced-Gas Flotation

Rotation of the rotor generates a liquid vortex resulting in a gas-liquid interface which extends through the interior of the rotor to a point just above the bottom of the cell. (Figure 6.22) The gas cavity within the vortex is at sub-atmospheric pressure resulting in the flow of gas from the vapor space in the cell through the rotor where it is mixed with the water.

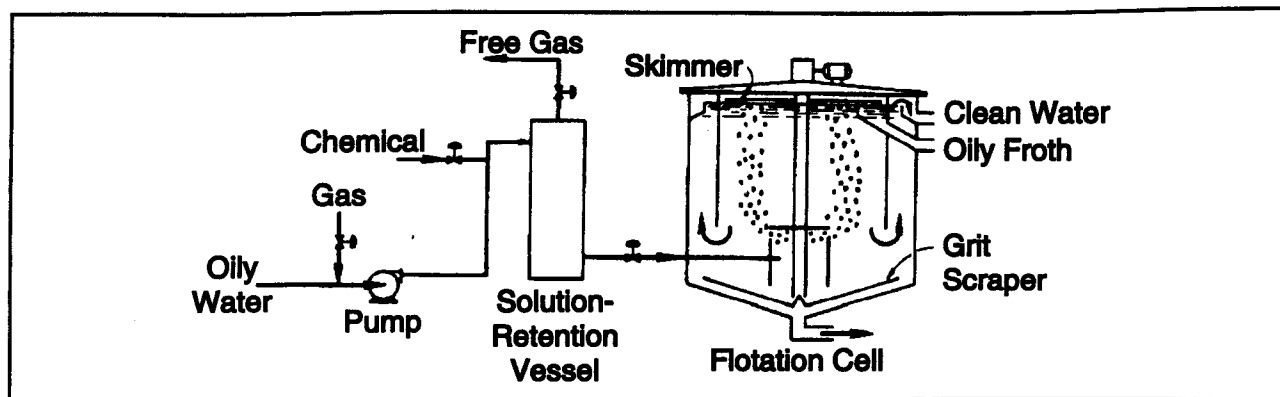


Figure 6.21 Full-Stream Dissolved Gas Flotation (Courtesy SPE)

Produced gas is used for flotation. A gas pressure of approximately 0.5 ounce (0.03 psig) [0.2 kPa] is maintained in the cell to prevent air entry.

Most rotor type induced gas units contain four separate flotation cells. The oily water flows through each of the four cells in series, and the oil and solids content is progressively reduced in each cell. (Figure 6.23)

Typical gas water ratios are around 35 ft³/bbl [6.25 m³/m³] at design throughput.^(6.23) However, since the total volume of gas dispersed in the water is not normally adjustable, water throughputs less than design result in substantially higher gas/water ratios.

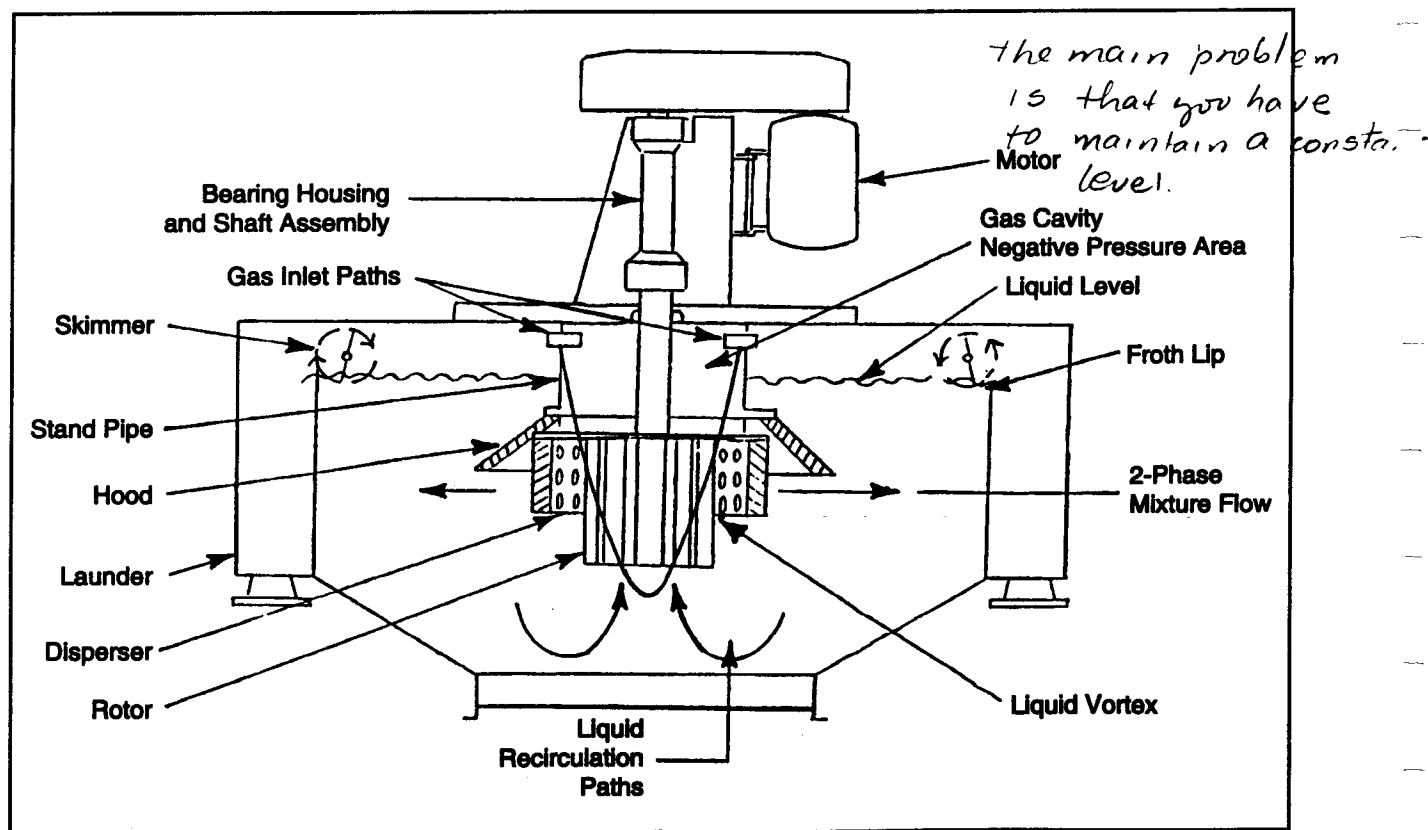


Figure 6.22 Cross Section of Rotor-Type Dispersed Gas Flotation Cell
(Courtesy Wemco Division, Envirotech Corp.)

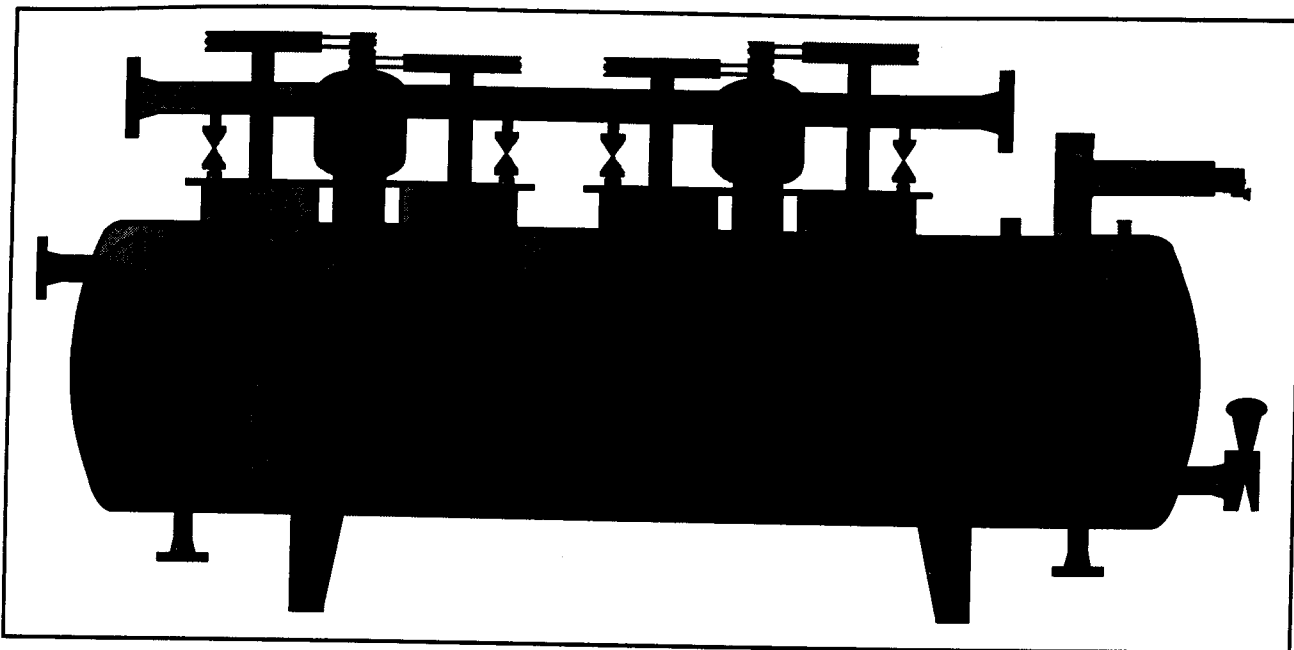


Figure 6.23 Four-Stage Dispersed-Gas Flotation Cell (Courtesy Natco)

2. Eductor-Type Induced-Gas Flotation

Clean water is pumped from the discharge of the flotation cell through an eductor in each cell as shown in Figure 6.24. This creates a localized low pressure area at the nozzle exit within the eductor. This causes natural gas to flow from the vapor space into the eductor where it mixes with the water as it leaves the nozzle. It works exactly like the air ejector shown in Figure 6.6, except that the pressure drop in the nozzle is achieved by pumping water through it rather than by pulling gas through the nozzle.

This type of unit typically uses less power and less gas than a rotor type unit. Gas/water ratios are typically less than 10 ft³/bbl [1.8 m³/m³] at design throughput.^(6.23) The volume of gas dispersed in the water is not adjustable in most commercial units, so throughputs less than design result in higher gas/water ratios.

Eductor type induced gas flotation units are available which contain one, three, or four cells. A four cell unit is shown in Figure 6.25.

One vendor supplies a unit which is housed in a pressure vessel and has no internal moving parts. (Figure 6.26)

The performance of gas flotation cells is influenced by many variables including the gas concentration, water salinity, pH, temperature, crude oil type, inlet oil concentration, and chemical flotation aids.^(6.24)

Induced-gas flotation cells are widely used offshore to remove dispersed oil from waters being discharged overboard. They are used infrequently in onshore water-injection operations. Induced-gas flotation cells are not bothered by suspended solids and are capable of removal efficiencies of > 90% if operated properly. They typically require careful attention and do not accept system upsets gracefully.

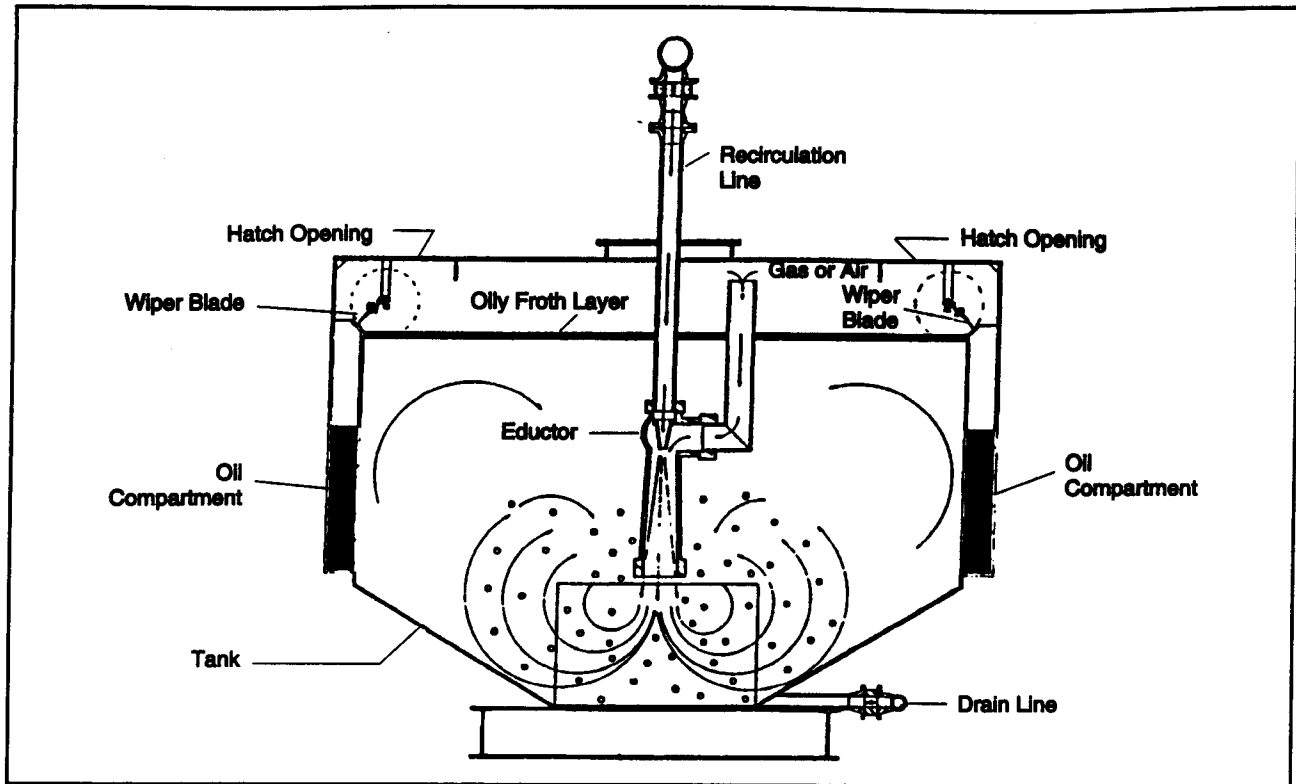


Figure 6.24 Cross Section of a Cell in a Multisep Induced-Gas Flotation (Courtesy Monosep, Inc.)

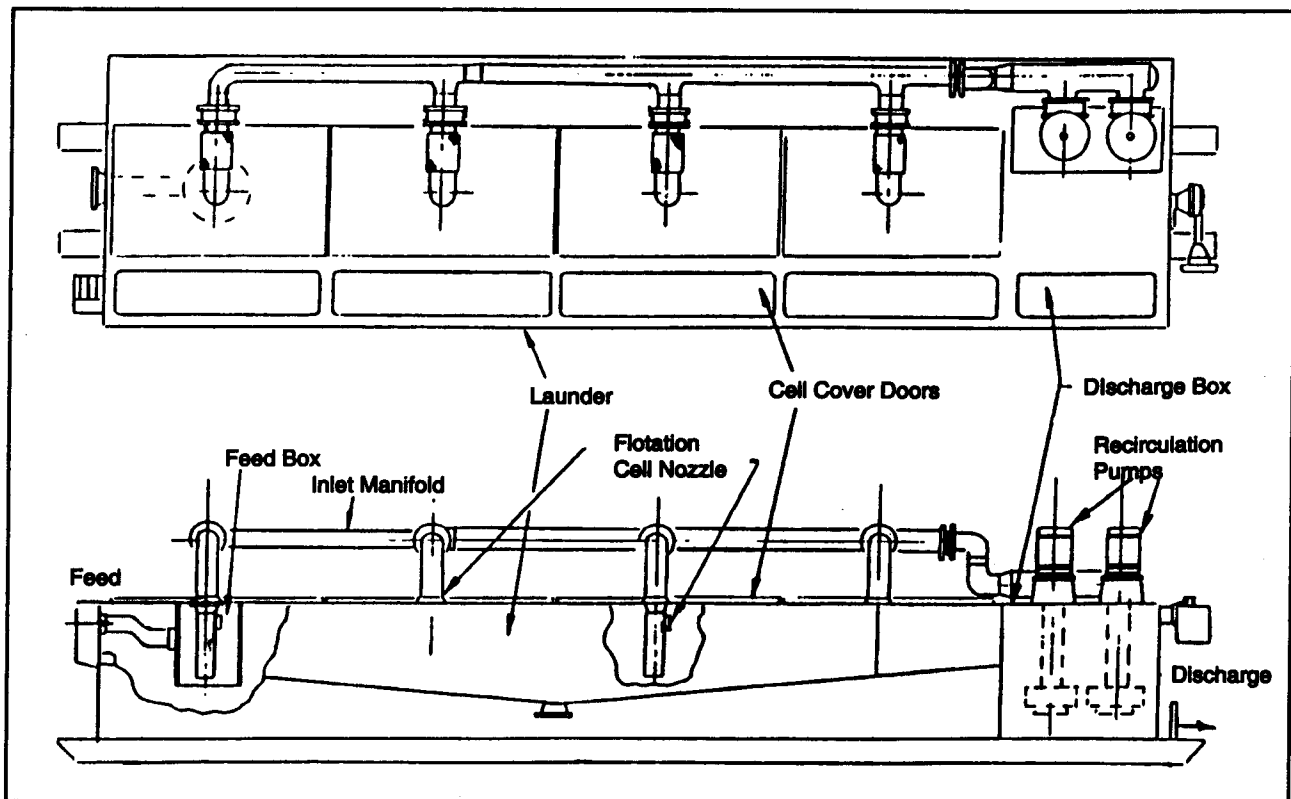


Figure 6.25 Nozzle-Type Four Cell Gas Flotation Cell (Courtesy Wemco Division, Envirotech Corp.)

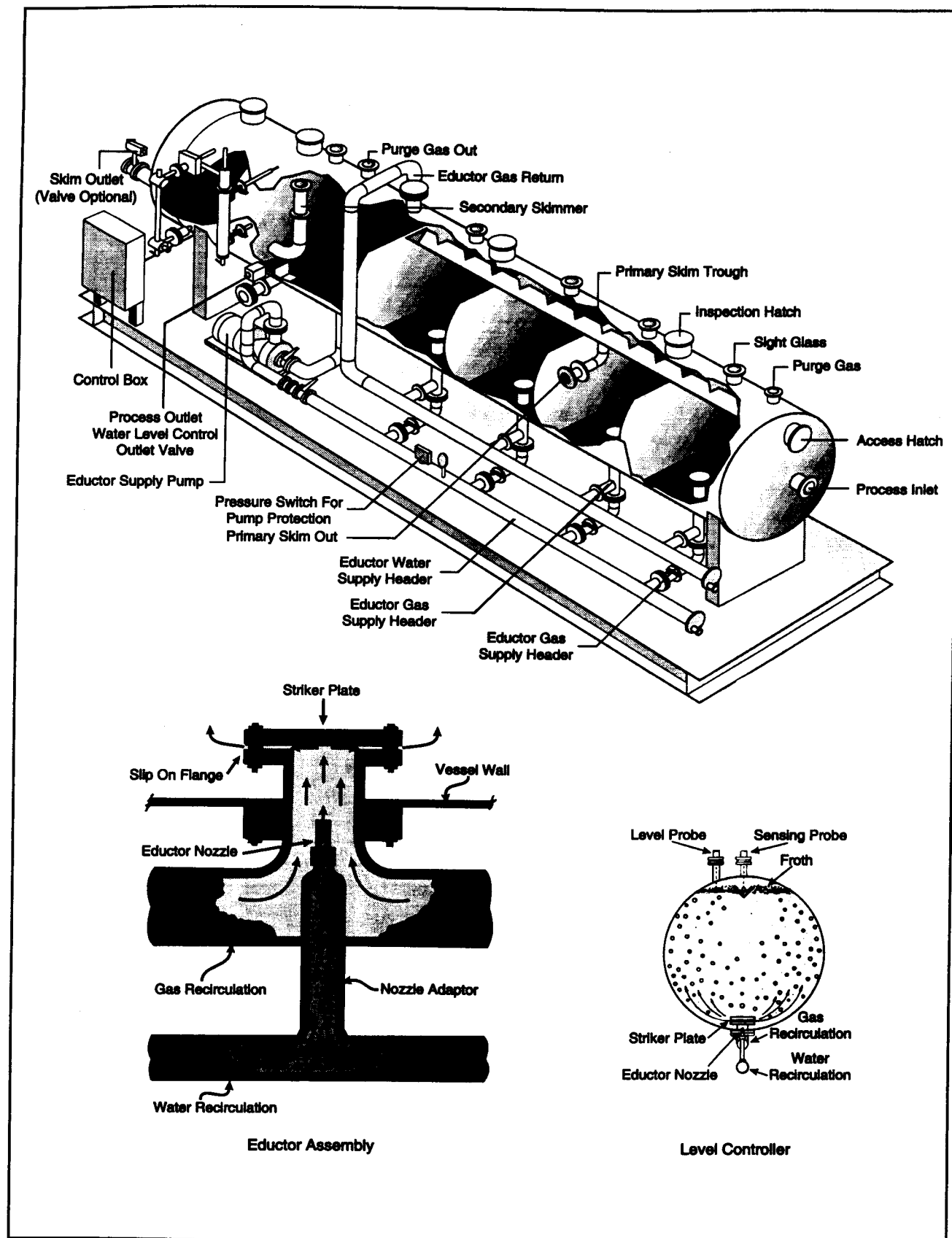


Figure 6.26 Induced Static Flotation Cell (Courtesy Envirotech Corp.)

Coalescers *(works well with oil + water + sand)*

Coalescing devices provide a solid surface which can be contacted and wet by small oil droplets. The droplets collect on the surface and coalesce into a continuous oil film. As the film becomes thicker, large drops of oil break loose due to gravity and/or fluid flow, and rise to the water surface.

Parallel Plate Separator

The parallel plate separator is a gravity separator. As the name implies, the parallel plate separator consists of a stack of tilted parallel plates approximately 4 to 10 cm apart. The oily water passes between the plates and free oil particles rise until they reach the underside of a plate where they collect and coalesce. (Figure 6.27) Any particle heavier than water will fall to the top of the plate below.

The coalesced oil travels upstream along the plate until it reaches the water surface where it is skimmed off and collected. Hence, the essential feature of a parallel plate separator is to reduce the distance an oil particle must travel before reaching a collection surface to a few centimeters.

The two basic types of parallel plate separators are the Parallel Plate Interceptor and the Tilted Plate Separator. When the plates are corrugated, the tilted plate separator is commonly referred to as a Corrugated Plate Separator or a Corrugated Plate Interceptor (CPI).

The plates in the Parallel Plate Interceptor are flat plates tilted at a 45° angle forming a series of chevrons as shown in Figure 6.28.

The CPI utilizes a stack of parallel corrugated plates. The entire plate pack is tilted at a 45° angle as shown in Figure 6.29. It is more commonly used in oil production operations than is the Parallel Plate Interceptor. It is a fairly efficient separator and occupies a modest amount of space, which makes it rather popular in installations where space is at a premium, such as in offshore production facilities.

Plate coalescing devices use closely spaced plates to reduce the distance the oil droplets have to travel. However, because of the close spacing, they are susceptible to plugging with solids.

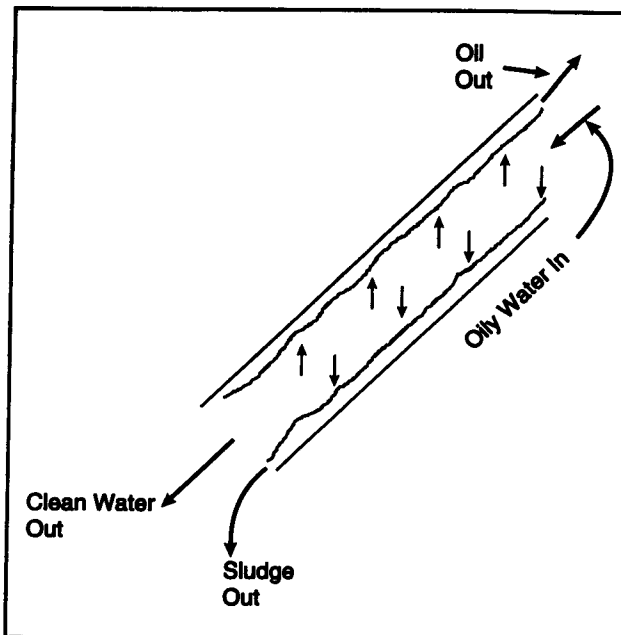


Figure 6.27 Parallel Plate

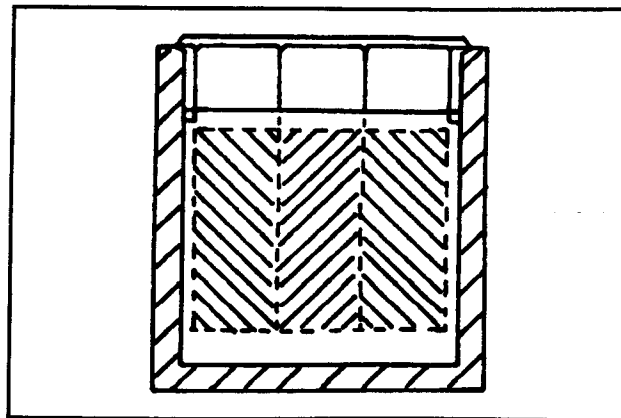


Figure 6.28 Parallel Plate Interceptor

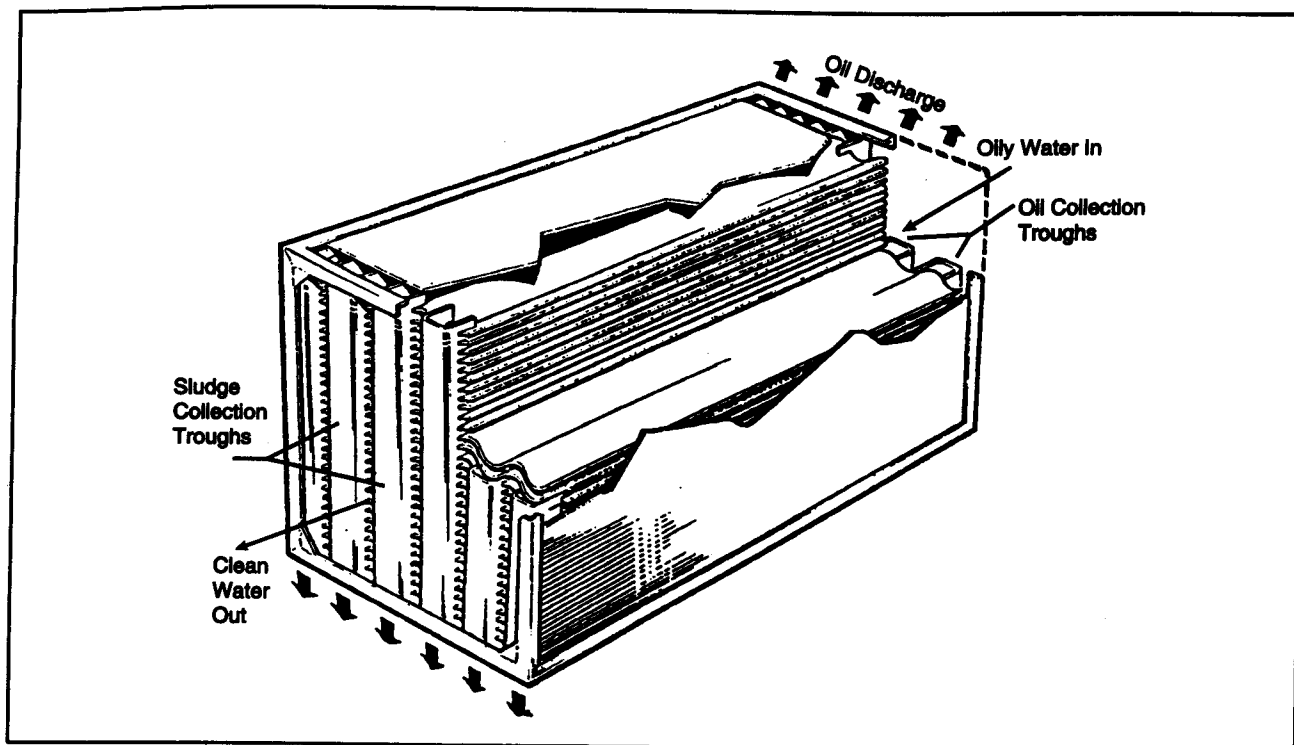


Figure 6.29 Corrugated Plate Interceptor (CPI)

Granular Media Coalescers

A granular bed coalescer is a vessel which contains a granular material with a large amount of surface area. As the oily water flows through the coalescing media, the finely dispersed oil droplets collect on the media surface and coalesce to form larger droplets. Once they become large enough the flow of water will displace them from the media and they will float to the surface of the water for collection.

Both upflow and downflow granular media coalescers are available. Three typical units are shown in Figures 6.30-6.32. The nut shell media filters discussed earlier (Figures 6.11 and 6.12) are also used as coalescers, as are the deep bed upflow, downflow, and dual flow filters. (Figures 6.10, 6.11, and 6.14)

These units gradually become saturated with oil, and must then be backwashed.

Oil Coalescing Filter Cartridge

Oil coalescing filter cartridges are also available. In the cartridge shown in Figure 6.33, flow is radial from the inside to the outside. Filter life is primarily determined by the suspended solids concentration in the water, as oil will not plug the cartridge.

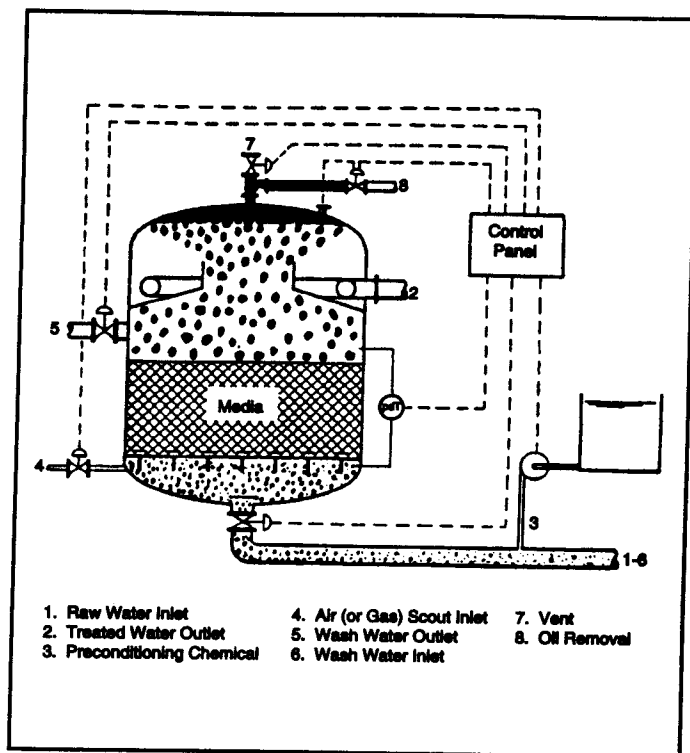


Figure 6.30 Upflow Colexer Coalescer
(Courtesy Infilco Degremont, Inc.)

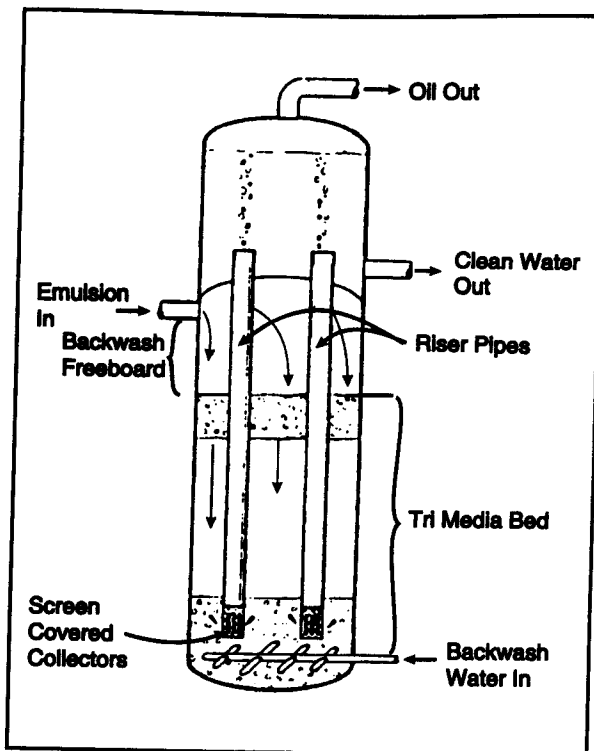


Figure 6.31 OSX Oil/Solids Downflow Coalescer
(Courtesy Natco)

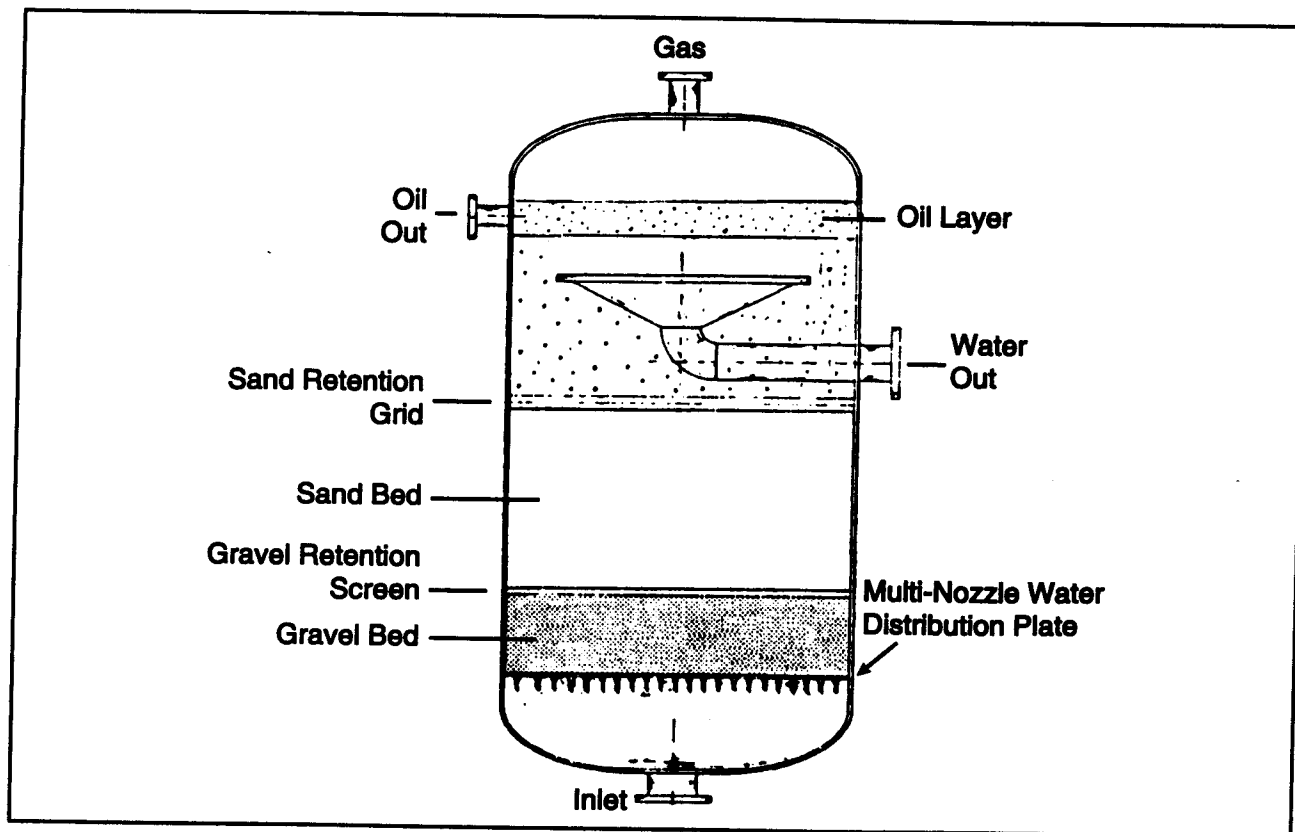


Figure 6.32 Oil Claire Deep Bed Upflow Coalescer (Courtesy US Filter)

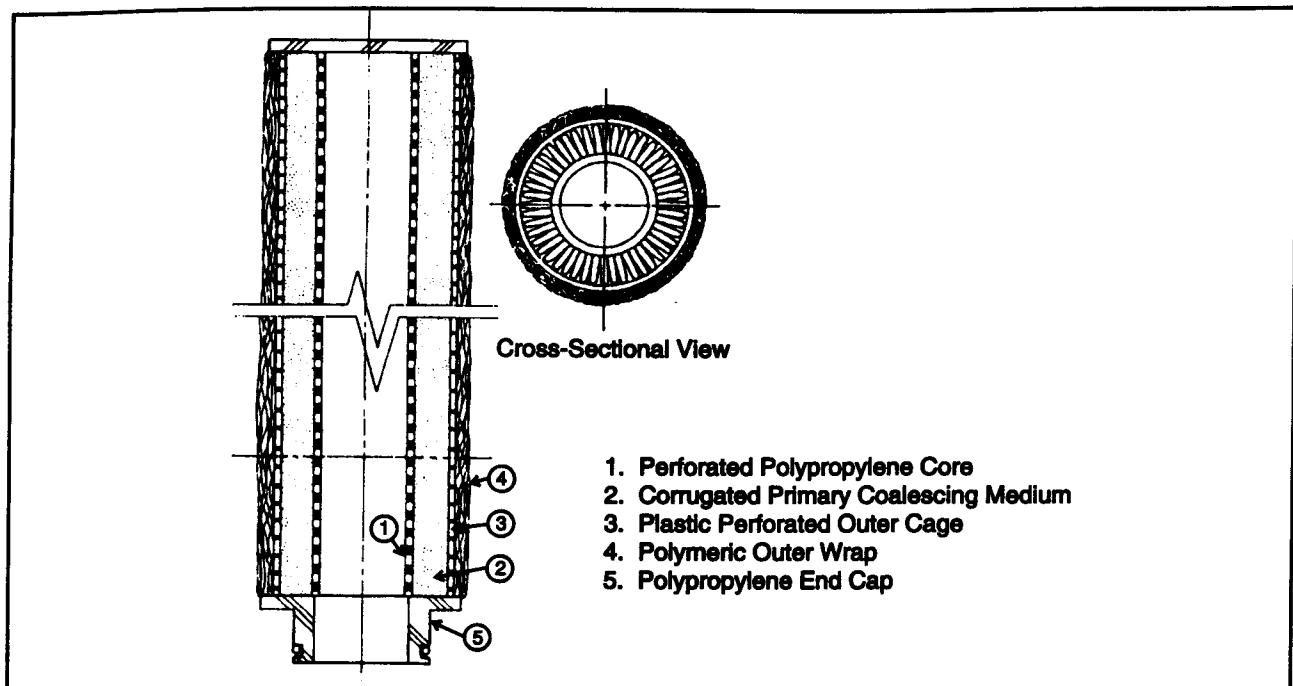


Figure 6.33 Oil Coalescing Filter Cartridge (Courtesy Pall Well Technology Corp.)

Hydrocyclones

A hydrocyclone is a device which multiplies gravity by as much as 2000 times, thereby accelerating the oil-water separation process.

A schematic drawing of a typical hydrocyclone designed to remove oil droplets from water is shown in Figure 6.34. Water is introduced tangentially through a rectangular port into a conically shaped chamber. The water rotates rapidly around the chamber and moves downward, exiting at the small end of the cone. As the water moves down the cone, the decreasing diameter causes the rotational velocity of the water to increase. This increases the centrifugal acceleration of the water (the denser fluid) toward the outer wall of the cone, and the centripetal acceleration of the lighter oil droplets towards the center of the cone. A slender core of oil (typically 1-2 mm in diameter) forms in the center of the cone, rises to the top and flows out of the hydrocyclone. This oily stream is called the overflow. The clean water exits from the bottom of the cone and is called the underflow.

Transit time through a hydrocyclone is typically less than one second.

The pressure drop across a hydrocyclone has typically been 50-100 psi [345-730 kPa] per stage. An additional 50-100 psig [345-730 kPa] back pressure must be applied to the underflow stream to collapse the air vortex and force the overflow stream to flow out the top. This translates into feed pressures of about 155 psi [1100 kPa] for a single stage unit. Because of the pressure requirements, the water must either be separated at high pressure or pumped. If a pump is required, it must be a special low-shear pump in order to minimize the creation of small oil droplets, which reduce separation efficiency.^(6.25)

In addition to units which operate at normal feed pressures are designs which operate at feed pressures of about 50 psi [350 kPa]. These units have capacities of 300-1000 bbl/day [48-159 m³/d] and offer excellent oil removal efficiency. The low feed pressure should significantly extend the range of applications of this technology.

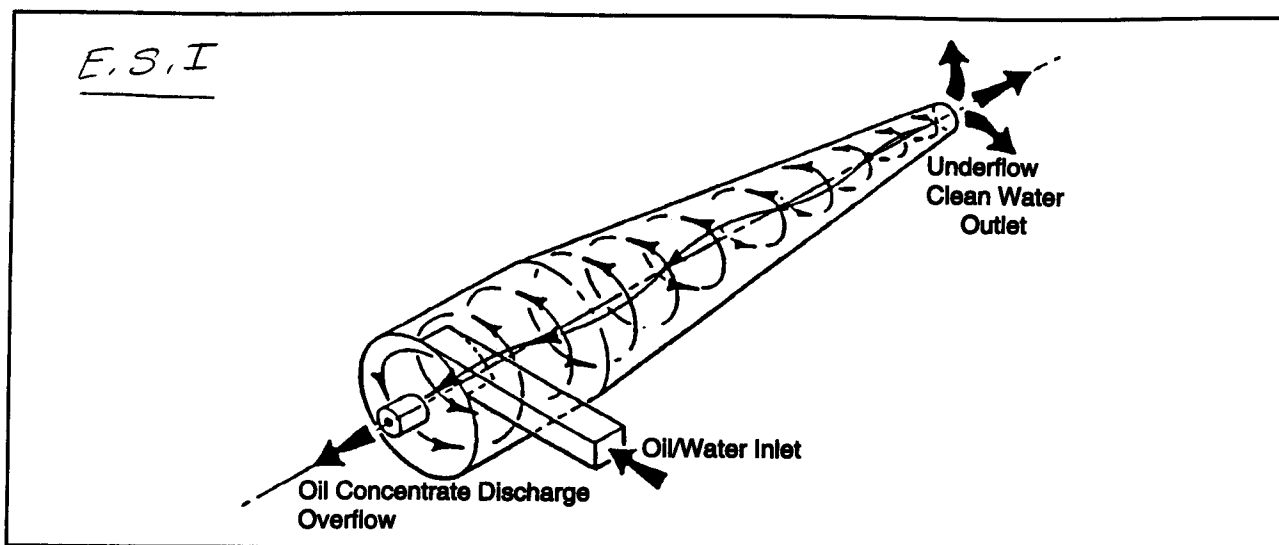


Figure 6.34 Oil/Water Hydrocyclone^(6.25)

Hydrocyclones are used primarily for the removal of oil from water in many offshore production operations.^(6.26) They are compact, insensitive to platform motion, and have no moving parts. Although hydrocyclones have seen little, if any, application in water-injection systems, they represent an important oil/water separation technology and are worthy of consideration when economically feasible.

Dynamic/Rotating Hydrocyclone (Centrifuge)

The principle of operation is exactly the same as the static hydrocyclone, except that an external motor is used to rotate the cyclone wall and the inlet vortex cone at 1600 to 3000 rpm.

As might be anticipated, the dynamic hydrocyclone has shown somewhat improved performance over a static hydrocyclone due to the increased gravitational forces. This is especially true for oil droplets with diameters less than 15 μm .

Increased rotational speeds will generate higher centrifugal forces, resulting in better oil-removal efficiencies at a given flow rate.

The potential for solids fouling is greater in the dynamic device than in the static units because of the low axial velocity (approx. 0.6 m/s) at the cyclone wall. Water-wet solids will migrate to the rotating wall, accumulate, then move toward the outlet. This may be a problem in waters with high suspended solids concentrations.

Centrifuges are quite expensive and are rarely used. However, several are in service in North Sea gas facilities for separation of oil from water prior to overboard discharge of the water.

WATER SOFTENING

The process of softening water is one where certain dissolved ions are removed from the water to prevent the formation of insoluble scales or deposits. Removal of calcium, magnesium, carbonate and bicarbonate ions from water are common examples of softening. Other ions may be removed if desired.

Raw water may be softened by three methods:

1. Precipitation softening
2. Ion exchange softening
3. Distillation

Each of these methods can be used independently or in combination to soften water. The choice of methods is influenced by the amount of softening required, the volume of water to be softened, and the installation and operating costs for the process selected.

Precipitation Softening

Precipitation softening refers to the removal of hardness and alkalinity by adding a chemical to the water which will combine with calcium, magnesium and bicarbonate ions and form an insoluble precipitate. Thus, hardness and alkalinity are removed from the water.

Lime and Lime-Soda Softening

The most commonly used chemicals are lime (calcium hydroxide) or lime plus soda ash (sodium carbonate).

When lime is used alone the process is called lime softening. Lime is added to the makeup water, causing an increase in pH. Calcium, carbonate, and bicarbonate ions are precipitated as calcium carbonate. If additional lime is added, magnesium ions will also be precipitated as magnesium hydroxide. Appreciable silica removal may also be realized due to adsorption on the magnesium hydroxide.

When soda is used along with lime, additional calcium is precipitated as calcium carbonate producing a lower hardness water. The process is referred to as lime-soda softening and may be classified as hot or cold depending on the temperature of the water.

Hot process softeners produce lower hardness and alkalinity than the cold process, and the reactions proceed more rapidly.^(6.27)

Hot lime-soda softeners can reduce the hardness of the water down to 15 to 25 ppm, while the cold process is limited to 30 to 50 ppm.^(6.28)

Caustic Softening

Caustic has also been used to reduce the hardness of high TDS waters from about 500 to less than 20 ppm in steamflooding operations in California.^(6.29) Sodium hydroxide is added to the water to raise the pH to about 9.3. Calcium and magnesium ions are precipitated as calcium carbonate and magnesium hydroxide.

This process offers significant capital and operating cost savings over a conventional weak-acid ion-exchange system, with an additional benefit of partial silica removal.

Compared with the lime process, it is said to be cost competitive, operationally more reliable, and offers the additional benefit of producing only about 20% of the solid sludge volumes produced by the lime process.

Ion Exchange Softening

Ion exchange softening is achieved by flowing the raw water through a vessel filled with small spheres (called beads) of a material referred to as an ion exchange resin. The resin beads are usually made from a synthetic plastic and are both permeable and porous. The porous beads contain many electrically charged sites throughout their structure to which are attached ions or ionizable groups of opposite charge.^(6,28)

As the raw water flows through the bed, the ions attached to the beads are replaced by ions from the water which have a higher affinity for the resin, and the ions originally attached to the resin are expelled into the water. Thus, ions in the raw water are exchanged for ions attached to the resin beads.

Once the bed is saturated with ions removed from the water, the bed may be regenerated by soaking it in a solution containing a high concentration of the ions originally attached to the resin beads. Ion exchange occurs once again, restoring the resin to its original condition.

Strong-Acid Ion Exchange Resins

A strong-acid cation exchange resin is usually a sulfonated copolymer of styrene and divinylbenzene. The resin functions by exchanging sodium ions for calcium and magnesium ions and is also referred to as sodium exchange softening. When water containing calcium and magnesium ions is passed through a bed of sodium exchange resin, the calcium and magnesium ions are removed from the water and replaced with sodium ions.

This system works well on oil-free water with TDS < 5000 ppm. When the TDS of the water is higher, sodium ions in the produced water compete with calcium and magnesium ions for sites on the resin. This makes it very difficult to reach hardness levels < 1 ppm, which are typically required for steam generators.

When the beads become saturated with calcium and magnesium ions, it is regenerated by washing with a strong solution of sodium chloride. The high concentration of sodium in the solution reverses the exchange process, replacing the calcium and magnesium ions on the resin beads with sodium ions, making them once again ready for use.

Weak-Acid Ion Exchange Resins

A weak-acid cation exchange resin is typically a carboxylic acid group within an acrylic divinylbenzene matrix. This type of resin exhibits a very strong selectivity for calcium and magnesium ions over sodium ions. Hence, it can produce very low hardness levels in brines and is commonly used to soften waters with TDS > 5000 ppm.

The resin is considerably more costly than the strong acid resin, and requires a two-step regeneration. Hydrochloric acid is first used to remove the calcium and magnesium; then it is treated with caustic soda (sodium hydroxide) to convert the resin back to the sodium form. The cost of this regeneration cycle is several times higher the brine regeneration required for strong acid resins.

The two-step regeneration cycle is necessary to prevent the production of an acidic soft water. If the resin is placed in service after being regenerated with acid alone, the resin will soften the water by exchanging hydrogen ions for calcium and magnesium ions, thus lowering the pH. This is avoided by conditioning the resin with caustic after acid regeneration. Sodium from the caustic exchanges with the hydrogen in the resin. Then, when the resin is placed in service, sodium ions are exchanged for calcium and magnesium ions.

Anion Exchange Resins

Other types of ion exchange units will remove anions from water. A weakly basic type will remove sulfate, chloride and nitrate. A strongly basic type will remove these ions plus silica, carbon dioxide, and sulfides.

Demineralization

Demineralization is accomplished by using a hydrogen exchanger to remove cations and an anion exchanger to remove anions. It is used to obtain high quality water when the raw water contains small quantities of dissolved solids.

Both the initial investment and operating costs are high, making it difficult to justify demineralization for most oilfield facilities.

Distillation

Distillation is the most expensive method of softening and is used primarily to remove dissolved solids from brackish waters to produce high quality feedwater. It is not widely used in oilfield installations.

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NOTES

WATER INJECTION SYSTEMS

A water injection system combines a process facility with a distribution system to produce and deliver water of a given quality to the injection wellbore. There are three primary goals from an operational standpoint:

1. Deliver clean water to the injection wellbore.
2. Prevent plugging and deposition of solids in lines, vessels and wells.
3. Maintain system integrity by preventing the corrosion of surface and downhole equipment.

Measurement of the chemical and physical characteristics of injection water is the basis for both design and monitoring of any water injection system. The measurement and importance of the majority of these characteristics have been previously discussed in this book. However, one topic remains to be addressed prior to an examination of system design and monitoring: water sensitive formations.

WATER SENSITIVE FORMATIONS

Clays which exist in sandstone formation rocks are in equilibrium with the connate or natural formation water. When these clays come in contact with injection water or treating fluids, reactions can take place between the clays and the injected fluid which may result in decreased permeability. In water injection projects, this type of formation damage occurs most commonly when the salinity of the injection water is significantly lower than that of the connate water.

Carbonate formations are seldom clay-bearing, and when clays are present, they are incorporated into the matrix. Hence, carbonate reservoirs are seldom subject to permeability reduction as a result of interactions between clays and injected fluids.^(7.1)

Nearly all sands and sandstones contain clays which may be present as part of the matrix, as a coating on the pore walls, or lie loose in the pores. Clays may also be present as thin layers in sand beds.

A combination of swelling and dispersion commonly referred to as clay blocking is considered the predominant mechanism of permeability reduction by injection of low salinity water.^(7.2) Slight swelling promotes loosening and mobility of fine particles from the pore walls. The particles are rearranged during fluid flow, and are trapped at the pore exits.

The most common clay mineral groups known to cause permeability damage to formations are the smectite group (of which the montmorillonites are the best known), kaolins, chlorites and illites.

These clays are constructed of particles which can adsorb water on their surfaces and edges and, in the case of montmorillonite, between the layers of the basic particle itself. This adsorption increases as water salinity decreases and results in clay swelling or dispersion.^(7.1)

Permeability reduction due to the hydration of montmorillonite is much greater than that due to the hydration of other clays. Dispersion of illite is less than montmorillonite, and least with kaolinite and chlorite.

In general, waters with salinities at least as great as those shown in Table 7.1 will cause little reduction in permeability as a result of clay swelling.

Strong acids (1.0 N HCl) and strong bases (0.5 N NaOH) can also cause clay swelling.^(7.3)

TABLE 7.1

Minimum Salinities of Brines Required to Prevent Clay Blocking in Water-Sensitive Formations^(7.1)

Clay Species	Concentration (ppm)		
	NaCl	CaCl ₂	KCl
Montmorillonite	30 000	10 000	10 000
Illite, Kaolinite, Chlorite	10 000	1 000	1 000

GUIDELINES TO SYSTEM DESIGN

Water Source Selection

The first step in selecting a water supply is to determine how much water will be needed. The source must be able to supply sufficient water to achieve the maximum desired injection rate for the project being considered.

A pilot flood is often instituted initially before expansion to a full scale flood. If this is done, the water source used for the pilot should be the same as would be used for the full scale flood. This will give you a valid index of the behavior of the water and offer a chance to work out the major problems before expansion.

Some of the common sources of water for a waterflood are:

1. Produced water.
2. Oxygen-free brine or fresh water from other subsurface zones (supply wells).
3. Surface water from oceans, lakes, ponds, streams or rivers.
4. Water wells which draw water from shallow aquifers. This type of water typically contains a few ppm of dissolved oxygen, but is not saturated.

Each of these sources present different potential handling problems. Often there is no choice to be made, as there is only one adequately sized source available. Also, it is often necessary to mix waters from several sources to achieve the desired volume.

A summary of the main items to be considered in water source selection follows.

Corrosion

The corrosivity of each water should always be *measured* if possible. If meaningful measurements cannot be made, then a "guesstimate" of the relative corrosivity of the various waters can be made if you know something about the pH, dissolved gases, and the salinity. Remember the importance of on-site measurements using fresh samples.

There are three reasons to maintain effective corrosion control:

1. To obtain an acceptable service life for the equipment.
2. To minimize the generation of suspended solids.
3. To prevent loss of water to the environment, primarily to avoid pollution.

The widespread use of carbon steel in injection systems is often a compromise choice, since most oilfield waters have a pronounced appetite for steel. Steel offers a combination of high strength, low cost and easy fabrication which is very attractive to a designer. However, many times the low initial cost is more than offset by the subsequent costs of corrosion control and injection-well damage. It is often possible to obtain adequate system life, but impossible to maintain the needed water quality due to contamination of the water by corrosion products.

Solids Generation

Corrosion products constitute the primary source of suspended solids generated within bare-steel injection systems. Suspended solids deposition in the injection system contributes to accelerated corrosion rates due to under-deposit corrosion, provides a hiding place for bacteria, and shields the pipe surface from contact with corrosion inhibitors and/or biocides. A dirty bare-steel system is difficult to keep in one piece.

Suspended solids which do not precipitate in the injection system contribute to poor water quality and injection-well plugging. Water quality often becomes the controlling variable in the selection of a corrosion control strategy when the purpose of the system is to deliver high quality water to the injection wellbore.

The degree of contamination resulting from the corrosion of steel is determined by the corrosion rate and the solubility of the corrosion product. Iron carbonate is quite soluble in most injection waters, and normally does not contribute to suspended solids. However, iron sulfide and ferric hydroxide are exceptionally insoluble and can create serious plugging and water quality problems.

Hence, solids generation is particularly difficult to control in naturally sour waters and in sweet systems where sulfate reducing bacterial activity and/or oxygen entry is significant. Sweet systems include deaerated seawater, produced water and supply-well water containing no initial H₂S.

Scaling Tendency

Scaling calculations should be made to determine the probability of scale formation from each water. Remember that on-site measurement of pH, HCO₃⁻ and CO₃⁼ are necessary for accurate calcium carbonate scale calculations.

Water Compatibility

If two or more waters must be mixed on the surface prior to injection, scaling calculations and compatibility tests should be performed. Also, the compatibility of the injection water with the formation water must be assessed to determine if scale problems are likely in the producing wells after breakthrough of injection water.

Suspended Solids

The suspended solids concentration, the particle size distribution, and the nature and composition of the solids all have an important influence on the plugging tendency of a water. These same parameters also strongly influence filter selection if filtration is required.

Water Quality

Water quality testing can be carried out on each water using membrane filters or core samples.

Bacteria

A bacterial analysis of all potential water sources should be made. However, it should be noted that bacterial problems can develop in injection systems using an initially sterile water. Systems are easily infected and bacterial growth can be extremely rapid.

Oil Content

Any produced water which may be a candidate for injection would be examined for oil content. Any oil in the water can result in decreased injectivity, especially when combined with suspended solids such as iron sulfide. Also, emulsion blocks can form in injection wells.

Formation Sensitivity

Some formations contain clays which swell upon contact with low salinity water. This can result in reduced permeability and injectivity. Tests should be conducted on core samples to determine if this is a problem when low salinity injection waters are used.

Types of Treating Systems

Water treating systems have historically been classified as closed or open.

Closed Systems

A closed system is one which is designed to completely exclude oxygen. Since oxygen is one of the primary troublemakers, all modern water injection systems are designed as closed systems, regardless of the water source.

Open Systems

In open systems no attempt is made to exclude oxygen. Although open systems were popular many years ago, they are no longer used.

One of the major reasons for their demise is the fact that most injection wells are equipped with carbon-steel casing strings. Hence, even if all surface facilities and the injection tubing strings are coated, lined, or built of corrosion resistant materials, the injection-well casing string below the packer will be exposed to oxygenated water, and will eventually be destroyed by corrosion. In addition, the exclusion of oxygen precludes the growth of aerobic slimes within the system, thereby eliminating a common cause of injection well plugging.

Hence, it is common practice to deoxygenate waters that initially contain dissolved oxygen, such as surface waters and shallow-well waters prior to injection.

Primary Problems

Each type of water presents a different set of problems. It is extremely risky to make many generalizations. The following statements briefly summarize some of the primary problems which might be anticipated with injection waters from different sources.

Seawater

1. Saturated with oxygen — very corrosive.
2. Contains suspended solids and marine organisms. Amount varies with location and depth. Should be filtered in most cases.
3. Contains aerobic bacteria and sulfate reducing bacteria.
4. Fouling must be prevented in the intake system.
5. Calcium carbonate scale often forms in the injection wells and in heat exchange equipment.
6. Contains a high concentration of sulfate. Calcium sulfate scale is not likely in the injection system. However, if the formation water contains sufficient quantities of barium, strontium or calcium, sulfate scale formation in the producing wells is likely after breakthrough of the injection water.
7. Reservoir souring is likely. Hence, the impact of H_2S on the design of producing wells and production facilities must be considered prior to construction.

Fresh Surface Water

1. Saturated with oxygen — corrosivity varies with water composition.
2. Normally contains suspended solids which must be removed. May be seasonally variable.
3. Aerobic bacteria are usually encountered, and it is not uncommon to find sulfate reducers growing under deposits in the system.
4. Downhole scale formation may be a problem, but is often minimal due to the low dissolved solids.
5. May be incompatible with the formation water.
6. Can cause clay swelling and loss of injectivity if formation contains sensitive clays.

Produced Water

1. Usually contains dissolved H_2S and/or CO_2 . Corrosivity varies.
2. Usually contains suspended solids. Corrosion product is most common solid.
3. Oil carryover is a frequent problem.
4. Various types of bacteria, including sulfate reducing bacteria, are often present.
5. Scale formation is possible. However, most scale problems are in the production system, and scale in the injection system is unlikely unless there are incompatibility problems due to mixing with another water prior to injection.

Subsurface Source Water

1. May not be very corrosive, depending on composition, providing it is free of dissolved oxygen. Oxygen leakage into source well annulus is a frequent problem. Water from shallow aquifers often contains oxygen.

2. May be scale forming. Normally a scaling water would not be used.
3. If sufficiently fresh, formation sensitivity must be considered.
4. Various types of bacteria, including sulfate reducing bacteria can be a problem.
5. May contain suspended solids. Normally this is not a problem, and most source waters do not require filtration.
6. Watch for incompatibility with formation water. The possibility of scale problems in the producing wells after breakthrough must be examined.

Typical System Designs

There are multiple approaches to process any water to a given specification. The following designs are typical.

Surface Waters

Both seawater and fresh surface waters should be deoxygenated prior to injection. Virtually complete removal of dissolved oxygen has proven to be an effective and economically attractive method of corrosion control. Corrosion inhibitors are not usually required.

Seawater Injection Systems

A typical seawater injection system is shown in Figure 7.1. A gas stripping tower and a gas-blanketed water storage tank can be substituted for the vacuum tower if an appropriate gas source is available.

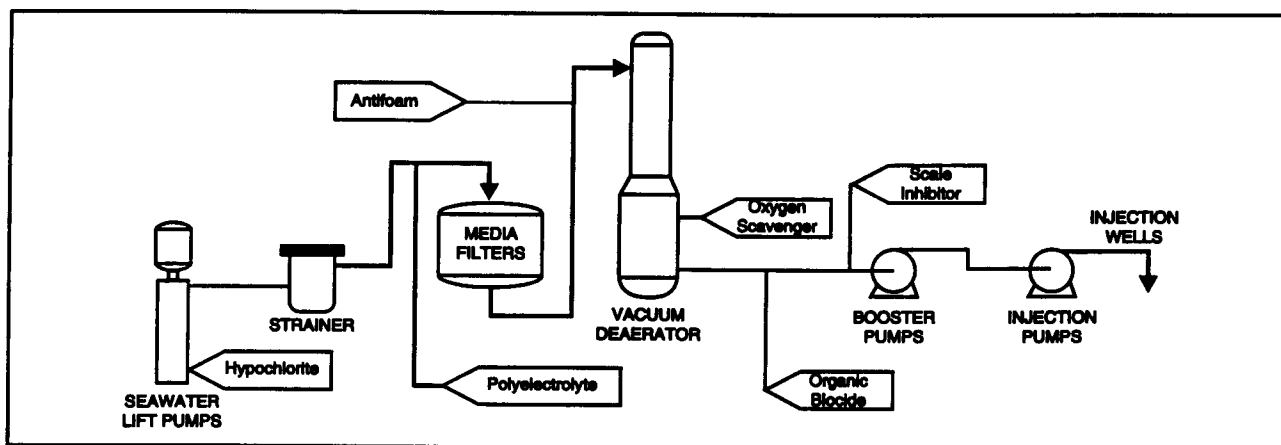


Figure 7.1 Typical Seawater Treatment System

Corrosion Control

Seawater is routinely deaerated prior to injection. Corrosion is controlled upstream of deaeration with lined steel or corrosion resistant materials and bare steel is used downstream of deaeration.

Work carried out by Conoco in the mid-1960's indicated that seawater containing oxygen levels less than 20 ppb [0.02 ppm] would corrode carbon steel at a rate of about 1 mpy as long as the pH remained around 8.^(7,4) It should be noted that velocities were less than 10 ft/s [3 m/s].

A mechanical deaeration tower employing gas stripping, vacuum deaeration or a combination, is employed to remove the bulk of the dissolved oxygen from the seawater. Levels as low as 15 ppb

[0.015 ppm] are possible in a properly designed tower using either process. Hence the choice of process is largely governed by practical considerations such as the availability of gas and its suitability as a stripping agent.

If dissolved oxygen concentrations in the water exiting the deaerator are higher than desired, the remainder is removed with a sulfite oxygen scavenger. Ammonium bisulfite is the current chemical of choice.

Although supplemental corrosion control downstream of deaeration is rare, a corrosion inhibitor can be continuously injected downstream of deaeration if necessary. A water-soluble inhibitor is used in order to eliminate any possibility of formation plugging. Internal coatings or linings could also be used in many systems but are seldom employed.

The equipment upstream of deaeration typically consists of lift pumps, piping and filtration equipment. Pump corrosion is controlled through the use of appropriate metallurgy. Plastic coated or cement-lined steel, fiberglass, and corrosion resistant metals such as copper-nickel alloys have been successfully used as piping materials. Filter and deaerator shells are constructed of internally coated or lined steel, and internals are made of corrosion resistant metals, such as stainless steel, or plastic.

Velocity Effects

Low velocities promote deposition of solids and bacterial growth in an injection system. A minimum velocity of 3 ft/s [1 m/s] is generally recommended.

Increased velocities accelerate mass-transfer-controlled corrosion reactions including corrosion by dissolved oxygen and oxidizing biocides. Hence, as velocities increase, corrosion rates in seawater containing 20 ppb [0.02 ppm] oxygen will eventually reach unacceptable values.

At still higher velocities, erosion occurs, increasing the rate of metal loss still further. Obviously, if the water is corrosive, the combined effects of erosion and corrosion can be devastating.

Erosion is usually a non-issue in injection systems where the water must be pumped considerable distances, as the pump horsepower required to overcome friction loss at higher velocities tends to be excessive. For this reason, velocities in excess of 10 ft/s [3 m/s] are rare in large injection systems with long injection lines. However, velocities in excess of 20 ft/s [6 m/s] are common in some offshore seawater floods where the distances are short and the volumes injected are large, and velocity-related corrosion does occur.

Preferential Weld Metal Corrosion

Preferential weld metal corrosion has been observed in a number of seawater injection systems in the bare carbon steel injection piping downstream of deaeration. Accelerated corrosion has been observed both in the weld metal and in the heat affected zone. Minor differences in chemistry between the weld material and the line pipe are considered the primary cause of this problem by several investigators. In particular, the amount of Ni, Cu and P in the weld material has been singled out as a cause of this type of attack.^(7.5)

In addition, velocity effects could be a substantial contributing factor in high velocity systems. The weld bead can induce localized turbulence prior to attack. As attack proceeds, a groove is created which will create turbulence and accelerate metal loss.^(7.6)

Biological Control

"Chlorine" (chlorine or a hypochlorite solution) is usually injected into the bottom of the lift-pump casing to control both marine fouling and bacterial growth upstream of deaeration. The resulting

hypochlorite ion (OCl^-) oxidizes bromide ions naturally present in the seawater to form hypobromite ion (OBr^-), which in turn kills fouling organisms and bacteria. A minimum residual is carried through the deaerator, where it reacts with the oxygen scavenger, if one is used. If dissolved oxygen levels are acceptable without the use of an oxygen scavenger, the residual chlorine will be carried through the system until it is consumed by oxidizable species such as iron.

The hypobromite ion is a strong oxidizer and can cause corrosion to a number of metals if added in excess. In addition, it reacts with oxygen scavengers which results in the need for a small additional amount of scavenger.

However, on the positive side, it accelerates the reaction rate between oxygen scavengers and low concentrations of oxygen, and increases the filtration efficiency of media filters.^(7.7)

An organic biocide, such as a glutaraldehyde, is batched downstream of oxygen scavenging to protect the remainder of the system.

At least one operator uses ultraviolet sterilization in addition to chlorination upstream of deaeration, supplemented by batch organic biocide treatment downstream of deaeration. The use of UV decreases the amount of organic biocide required.^(7.8)

As might be anticipated, bacterial problems are more severe in large systems where the injection wells are several miles from the water treatment plant, such as in the Middle East. Bacterial control is considerably more challenging in these systems, and pigging of long injection lines is an extremely important element in the overall microbial control strategy.

In compact offshore injection systems, the distance from deaeration to the injection wells is often a matter of feet. Bacterial control is not a major challenge in these systems from the standpoint of corrosion. However, there is considerable concern about reservoir souring due to SRB activity in the injection water, and strict microbial control is considered mandatory.

Scale Control

Seawater may form calcium carbonate scale in the injection wells. If scale formation is anticipated, a scale inhibitor should be injected upstream of the injection pump. If injection rates are extremely high, the water may not warm up enough by the time it reaches the bottom of the injection wells to require inhibition.

Water Quality

Filtered, deaerated seawater typically contains less than 0.5 mg/L suspended solids when it leaves the treatment plant. In short systems, the water arrives at the injection wellbore with very little deterioration in quality. However, in systems that stretch over several miles, contamination of the system by sulfate reducing bacteria is virtually certain. Effective bacterial control in large systems is a formidable challenge, and typically requires significant quantities of biocide and frequent pigging.

Corrosion damage due to sulfate reducing bacterial activity can be controlled sufficiently to guarantee a long life for the injection system. However, even low corrosion rates generate sufficient iron sulfide to reduce water quality by the time it reaches the injection wells. Even so, it should be noted that in the vast majority of seawater injection systems, the quality of the water is markedly superior to the quality achieved with most produced water systems.

Monitoring

Sample points should be located between every piece of equipment and the system should be equipped with adequate instrumentation to monitor corrosion and water quality parameters.

Fresh Surface-Water Injection Systems

Rivers are the most common source of fresh surface-water for injection, although lake water has also been used. A typical river water injection system is shown in Figure 7.2. A vacuum deaerator is often substituted for the gas stripping tower when stripping gas is not available.

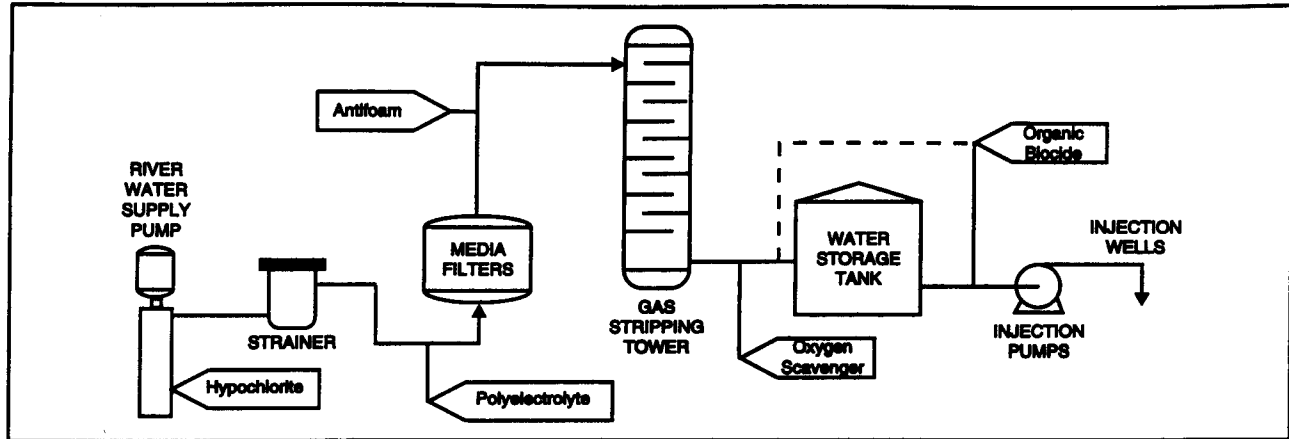


Figure 7.2 Typical River Water Treatment System

Comments:

1. The water storage tank should be equipped with a gas blanket.
2. The filters, gas stripping tower, and water storage tank should be internally coated and equipped with sacrificial anodes.
3. A vacuum tower can be substituted for the gas stripping tower if desired.
4. Bacterial problems upstream of deaeration may be dealt with by continuous chlorination at the supply pump intake. Re-treatment downstream of the oxygen removal step with an organic biocide is normally required. Since many biocides are incompatible with oxygen scavengers, the normal injection point for the organic biocide is downstream of the water storage tank. Provision should be made for periodic slug treatment of the tank as needed.
5. If the water is expected to form scale in the injection wells, a scale inhibitor should be injected upstream of the injection pump.
6. Sample points should be located between every piece of equipment.

Subsurface Waters

Produced-Water Injection Systems

A typical produced-water treatment system is shown in Figure 7.3. Many produced waters are not filtered prior to injection.

Sweet Systems

In sweet systems, carbon steel can be used in conjunction with effective corrosion inhibition, *provided that oxygen entry and sulfate reducing bacterial activity can be adequately controlled.*

Corrosion rates can be maintained at very low values with corrosion inhibitors, and most of the iron resulting from the residual corrosion will be soluble. However, sulfate reducing bacterial growth

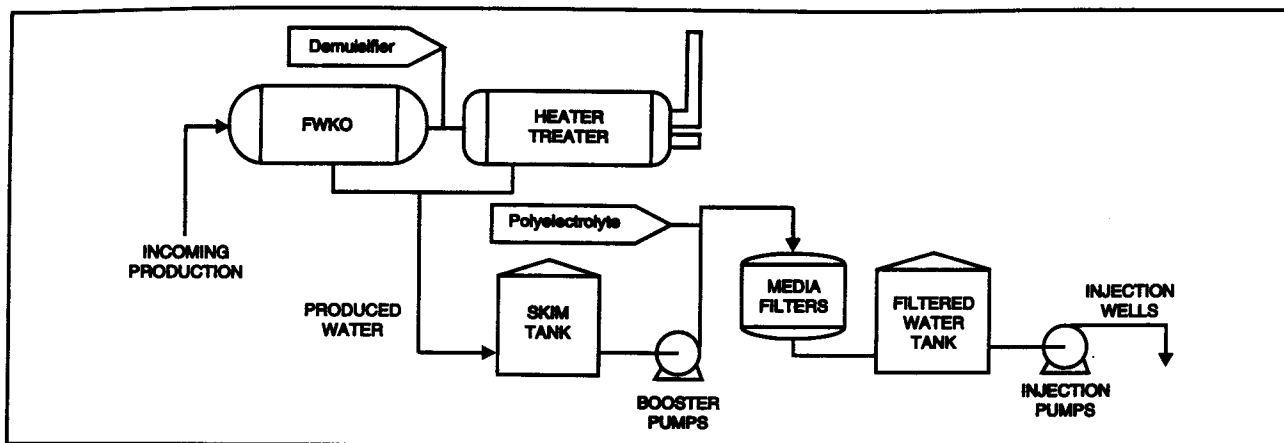


Figure 7.3 Typical Produced Water Treatment System

and/or oxygen entry will result in the generation of insoluble sulfides or hydroxides which can seriously reduce water quality.

Corrosion rates, bacterial counts, and oxygen concentration must be carefully monitored. Continuous injection of a water soluble corrosion inhibitor can control CO₂ corrosion; however, corrosion inhibitors are ineffective against oxygen corrosion.

It is preferable to exclude oxygen through careful maintenance of gas blankets and pump seals, and prompt leak repair. Oxygen scavengers can be employed if necessary. A maximum oxygen concentration of 5 ppb [0.005 ppm] is recommended.

Filters and water storage tanks should be internally coated and equipped with sacrificial anodes.

Batch treatment with an organic biocide is the norm if bacterial control is necessary.

Velocities should be maintained in excess of 3 ft/s [1 m/s]. Pigging of main lines and regular cleaning of vessels is strongly recommended. Minimization of solids deposition in an injection system will decrease the severity of corrosion and bacterial problems and help to maintain good water quality.

Continuous injection of a scale inhibitor will be required if scale formation occurs in the injection wells.

The use of non-metallic piping or coated or lined steel makes good sense in sweet systems because it reduces the impact of bacteria and/or oxygen entry, which are extremely difficult to control.

Oil carryover is a very common problem. If so, an oil removal unit, such as a flotation cell, may be required upstream of filtration.

Sample points should be located between every piece of equipment and the system should be equipped with adequate instrumentation to monitor corrosion and water quality parameters.

Sour Systems

Carbon-steel systems handling sour waters will generate substantial amounts of insoluble corrosion iron sulfide, even if effectively inhibited.

The total amount of iron sulfide generated by corrosion can be approximated using the following equation:

$$W = 0.25 \times I.D.(in.) \times L(mi) \times mpy \quad (7.1)$$

Where:

- W = Weight of FeS Generated, lb/day
- mpy = general corrosion rate, mils/yr
- ID = internal diameter, inches
- L = line length, miles

For example, a 4-inch diameter injection line corroding at a rate of 5 mpy [0.13 mm/y] will generate 5 lbs [2.3 kg] of FeS *per mile* of pipe *each day*. This corrosion rate is quite acceptable in the absence of serious pitting from the standpoint of system life. However, the quantity of suspended solids generated is excessive.

The maximum possible concentration of iron sulfide in the water is dictated by the flow rate, the corrosion rate, and the steel surface area exposed to the water. It can be calculated using Equation 7.2.

$$Fes(mg/L) = \frac{693 \times I.D.(in.) \times L(mi) \times mpy}{BWPD} \quad (7.2)$$

It should be noted that only a portion of the iron sulfide generated by corrosion will end up as suspended particles in the injection water. Part of the corrosion product generated will remain attached to the pipe wall.

If the system is truly sour, and contains several hundred ppm H₂S (as in West Texas), sulfate reducing bacteria are unlikely to be a problem. However, microbiologically influenced corrosion has been implicated in at least one sour waterflood.^(7.9)

Oxygen exclusion is a must in a sour, bare-steel system. Even a small amount (5 ppb or more) can drastically accelerate corrosion. Conventional corrosion inhibitors are ineffective against oxygen entry and oxygen scavengers do not work well in sour systems. Hence, if oxygen enters the system, serious problems are likely.

The bottom line is that carbon steel cannot be used to handle sour waters if high quality water is required, even with good inhibition. Non-metallic materials or internally coated or lined steel should be used to the maximum extent possible.

Shallow Oxygenated Supply-Well Injection Systems

A typical water treatment facility for oxygen-containing water produced from shallow water supply wells is shown in Figure 7.4.

Comments:

1. The water storage tank should be equipped with a gas blanket.
2. Both water storage tanks should be internally coated and equipped with sacrificial anodes.
3. A biocide and/or scale control chemical may be required.

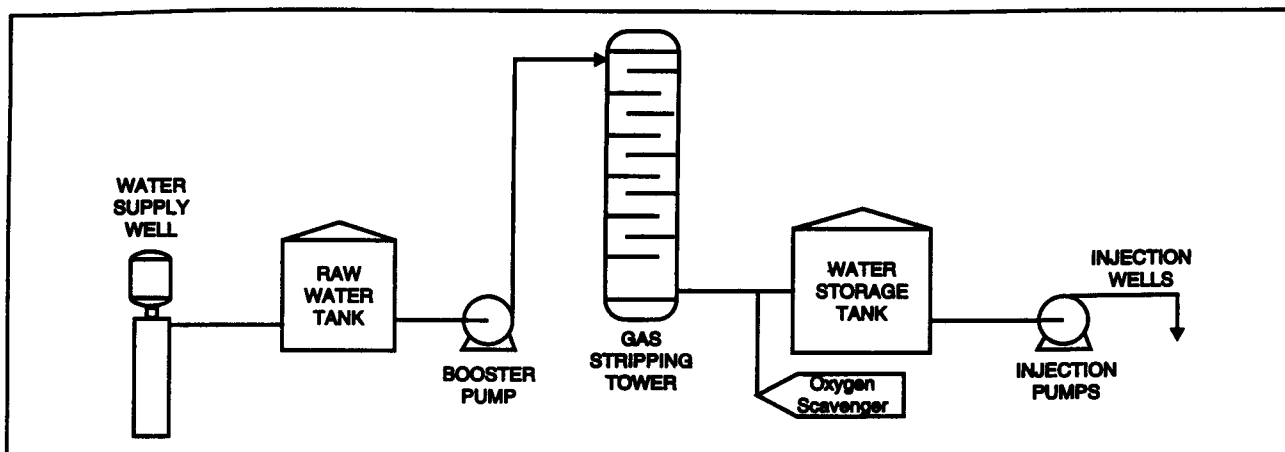


Figure 7.4 Typical Treatment Plant for Oxygenated Supply-Well Water

4. Water from supply wells rarely requires filtration.
5. Sample points should be located between every piece of equipment.

Oxygen-Free Supply-Well Injection Systems

If the water from the supply wells is oxygen-free, then the raw water tank, booster pump, gas stripping tower and oxygen scavenger can be deleted.

Conclusion

Many existing systems are variations of the typical systems outlined in the preceding paragraphs. Many are complex combinations of several systems. In most cases complex systems are the outgrowth of expansion, poor planning, or the failure to recognize the potential problems during the design phase.

The simpler the system, the better the chance that it can be operated successfully. Most waters can be treated with reasonably simple systems if sufficient emphasis is placed on identification of potential problems and careful planning during design.

WATER INJECTION SYSTEM INSPECTION AND ANALYSIS

Once you have completed the system and injection is underway, a systematic monitoring program should be instituted immediately. If problems are spotted early, they can be rectified before too much damage is done.

Inspection and Analysis Techniques

One of the best ways to spot problems is to start at the water source and go completely through the system to the injection wells, making appropriate measurements at selected sample points. Trends in certain data point out areas of the system which require further investigation.

Iron

An increase in iron content in the water through the system indicates corrosion. A decrease in iron content indicates deposition of iron compounds.

Calcium, Barium, Strontium

A decrease in the concentrations of any of these ions indicates a possibility of scale formation.

Bicarbonate, Carbonate

A decrease in the concentrations of these ions indicates deposition of CaCO_3 unless the pH is changing.

Sulfate

A decrease indicates sulfate scale deposition.

Temperature

Changes in temperature effect scale formation and corrosion rates.

Scaling Calculations

Actually, a complete water analysis should be carried out at each sample point. Then the CaCO_3 and the sulfate scaling tendencies can be calculated at each point. Changes through the system will point out possible scaling areas.

H_2S

An increase in H_2S concentration through the system (especially when the concentrations are at low levels) indicates the presence of sulfate reducing bacteria. A decrease in H_2S through the system indicates the presence of oxidizing agents in the system. (Air?)

Suspended Solids

An increase in suspended solids can be indicative of corrosion, scale formation, or bacterial activity. The solids should be analyzed to help determine the nature of the problem. A decrease in suspended solids indicates deposition.

Turbidity

Increased turbidity indicates increased plugging solids which could be caused by a number of things. Decreased turbidity indicates deposition.

Water Quality Measurements

Another measurement of plugging solids. The material on the membrane filter should be analyzed to determine the nature of the solids.

Corrosion Rate Measurements

Measurements should be taken throughout the system. In a closed system, an increase downstream of a given point could mean oxygen entry or bacterial activity.

Oxygen Concentration

Oxygen concentration measurements should be taken throughout the system. This is especially important in a closed system in order to pinpoint any oxygen entry point.

Oil Carryover

In produced water systems, the water coming from the treater should be checked for oil content. Measurements should also be taken upstream and downstream of all separation vessels.

Pump lubrication oil is a very common source of oil contamination in all types of systems.

Filter Operation

Suspended solids, turbidity and particle size distributions should be measured upstream and downstream of filtration as a function of time. Make sure the filter is doing its job and that it is backwashing properly.

Bacteria Counts

Counts of sulfate reducing bacteria and general bacteria should be taken through the system.

Visual Inspection

Remember that most of the measurements that are taken are problem indicators. If the data indicates that a certain problem is likely, the next step is to establish whether or not the problem *actually* exists. Visual inspection is the most reliable method.

Look for signs of trouble. Ask questions, get nosy and use your eyes. Check the gas blankets and the anodes in the vessels and make sure they are working. Look for leaky pump packing or any signs of oxygen entry. Any leaks? Are the meters plugging? Are the cartridge filters plugging frequently? With what? What about the wellhead injection pressures? Has it been necessary to acidize frequently to keep injection pressures down?

One of the key points to this approach is that it is to be done on a regular basis. It should be performed just like a preventive maintenance program. Do it whether you think it needs it or not.

On a new project, it would be wise to conduct a system survey at least quarterly. If things are running smoothly, the inspection frequency could be cut to once every six months. In no case should a system go longer than a year without a complete checkup. Conditions have a way of changing as a system ages.

Presentation of Results

Graphical presentation of many of the results obtained in such an inspection has been found to be most helpful, both in analyzing problems, and in conveying information to others.

An example of a suggested format is shown in Figure 7.5.^(7.10) Only three variables are shown plotted. Any of the other variables discussed could also be plotted. In addition, remember that this is data plotted as a function of distance through the system. A separate sheet is made for each inspection. Plots of any of the variables as a function of time can be made from this data.

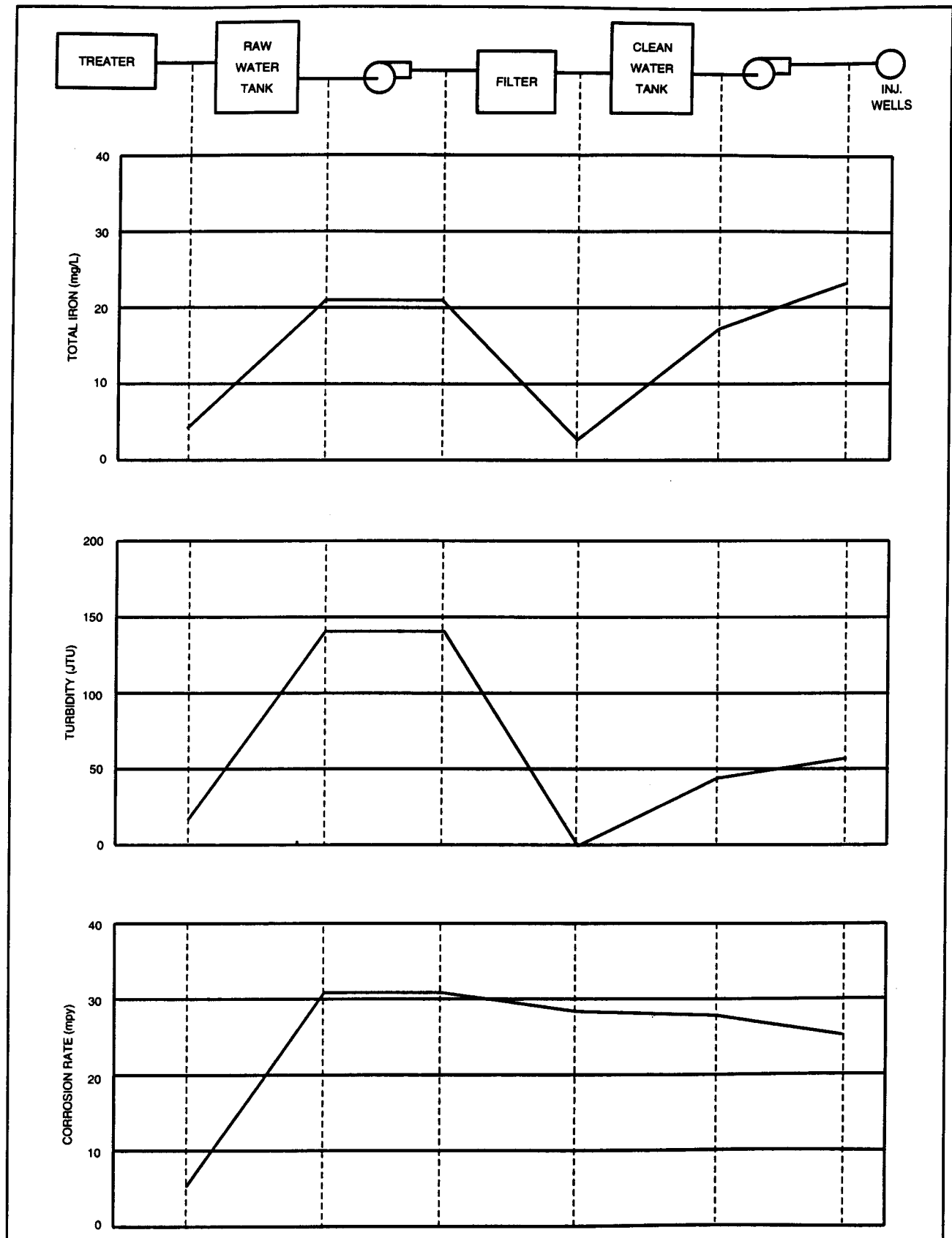


Figure 7.5 System Profiles

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8

WATER DISPOSAL SYSTEMS

The disposal of produced water can be classified into two categories: surface disposal and subsurface, or deep-well, disposal. The vast majority of surface disposal of produced water occurs offshore, where the water is discharged into the ocean.

SUBSURFACE DISPOSAL

Pollution of surface water supplies or fresh water aquifers has become a serious concern in recent years. This concern has focused attention on subsurface disposal as an economically attractive means of disposal of liquid wastes without polluting potable water supplies.

Subsurface disposal of liquid waste has been practiced by the petroleum industry since the early 1920's. Today it is common practice in many areas of the country, and several hundred thousand barrels of industrial wastes are being injected into subsurface formations each day. In addition to oil field brines, plant waste solutions containing such diverse components as acids, caustics, inorganic salts, and hydrocarbons are routinely injected into the ground in the oilfield.

The evolution of stringent requirements by several governmental agencies has added further incentive to consideration of subsurface disposal. As individuals, we are all vitally interested in maintaining the quality of our waters. However, as members of industrial organizations concerned with waste disposal at minimum cost, meeting these water quality criteria represents a tremendous technological and economic challenge. Since many waste streams can be successfully injected into the ground with a minimum amount of pre-treatment, subsurface disposal is becoming increasingly attractive from an economic standpoint.

Produced Water Disposal

The composition and characteristics of brines and fresh waters used in water injection systems have been previously discussed in detail. The same rules apply to the disposal of these waters. A brine disposal system should be designed, constructed and monitored in exactly the same manner as a waterflood injection system.

The primary difference between injecting water into the ground to dispose of it rather than to increase oil recovery, is that the water in disposal wells doesn't return to the surface as it does in waterfloods following breakthrough. The principal operational differences are twofold:

1. Incompatibility

Incompatibility between the injection water and the formation water is no longer a concern. Mixing between the two waters is minimal, and the radial movement of the mixing zone spreads any precipitate formed over a very large volume of reservoir rock. Hence, reservoir plugging as a result of mixing injection water and connate water is non-existent.

2. Reservoir Souring

Although often associated primarily with seawater floods, reservoir souring is a potential problem in any sweet water-injection system. Additional corrosion problems, sulfide cracking and hydrogen blistering in the production facilities are potentially catastrophic problems brought about by reservoir souring. In addition, the gradual souring of produced fluids after the breakthrough of sour injection water may render the produced gas unsaleable unless sweetening equipment is installed.

This is not an issue in water disposal wells.

Plant Water Disposal

The disposal of gas processing plant waters presents some slightly different problems because the composition of plant waste water is usually quite different from a waterflood injection water. However, the same basic rules apply and common sense is still the rule of the day.

Gas plant waste waters are a mixture of many different streams.

1. Cooling Tower Blowdown
2. Boiler Water Blowdown
3. Ion Exchange Bed Regeneration Streams
4. Filter Backwash
5. Produced Water (Fresh or Brine)
6. Cleaning Solutions — Acids, Caustic, Detergents
7. Corrosion Inhibitors and Biocides

These streams are usually fed to a common holding pond or evaporation pit prior to treatment and disposal. The holding pond should be lined to prevent soil pollution. It should be equipped with a high-level alarm to warn against overflow. An emergency overflow pit is also worthy of consideration.

One characteristic of plant waters is the cyclic nature of many of the streams. Blowdown, backwash and regeneration streams are all cyclic. Of course, the average composition of the pit water will be constant, but there will be variations in the composition of the water entering the disposal system as a function of time, depending on the frequency and amount of each stream and the size of the pond.

The composition of the pond water may change drastically during turn-around due to the discharge of large amounts of acid and other cleaning solutions.

The following guidelines are suggested in the examination of plant waters:

1. Determine the composition and amount of each stream entering the holding pond.
2. If it is a cyclic discharge, determine the discharge period and frequency.
3. Determine the corrosivity, suspended solids, and compatibility of the various streams.

These factors will enable you to select the proper materials, determine the needed pond capacity and predict incompatibility problems. For example, if produced brine containing a large amount of

calcium is commingled with the regeneration backwash from a hydrogen zeolite bed, severe scaling problems may occur in the disposal system. Sulfuric acid is commonly used to regenerate hydrogen zeolites, and the regeneration backwash contains a high sulfate concentration. Calcium sulfate scale would be quite likely if these two streams were commingled. One solution would be to use hydrochloric acid to regenerate the bed rather than sulfuric acid and eliminate the sulfate ion. However, HCl is more expensive than H_2SO_4 .

A second alternative would be to prevent commingling of the two streams by discharging them into separate ponds. The ponds could then be pumped down on an alternate basis. It is often advisable to look at the possibility of grouping the various streams into compatible groups and put them in separate ponds. Each pond can then be injected sequentially with no mixing problems. This can prevent or minimize scaling and decrease the filtration load.

Open or Closed System?

Although open systems are almost never used in water injection systems, they are sometimes the most practical solution to the disposal of aerated waste waters. The primary challenge is to complete the disposal well(s) in such a way that the tubular goods below the packer will be protected against corrosion. Corrosion resistant alloys, non-metallic materials such as fiberglass, or plastic-coated steel have all been used.

SURFACE DISCHARGE

Offshore Disposal

In most countries, water produced in offshore production operations must be processed to reduce the oil and grease content to levels acceptable to local regulatory agencies. Although the toxicity of the discharged water is of concern in some areas, removal of dispersed oil prior to discharge is often the sole process applied to this type of water.

There are four oil removal processes commonly used for this purpose:

1. Skim tank
2. Corrugated plate interceptor
3. Induced gas flotation cell
4. Hydrocyclone

These processes may be applied individually, or in combination to reach the desired result. Typical process designs are shown in Figures 8.1 and 8.2.

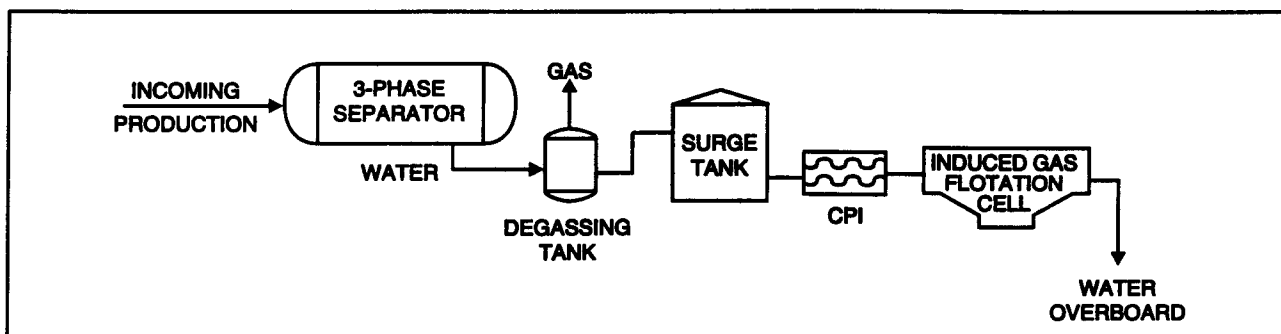


Figure 8.1 Typical Offshore Produced Water Treatment

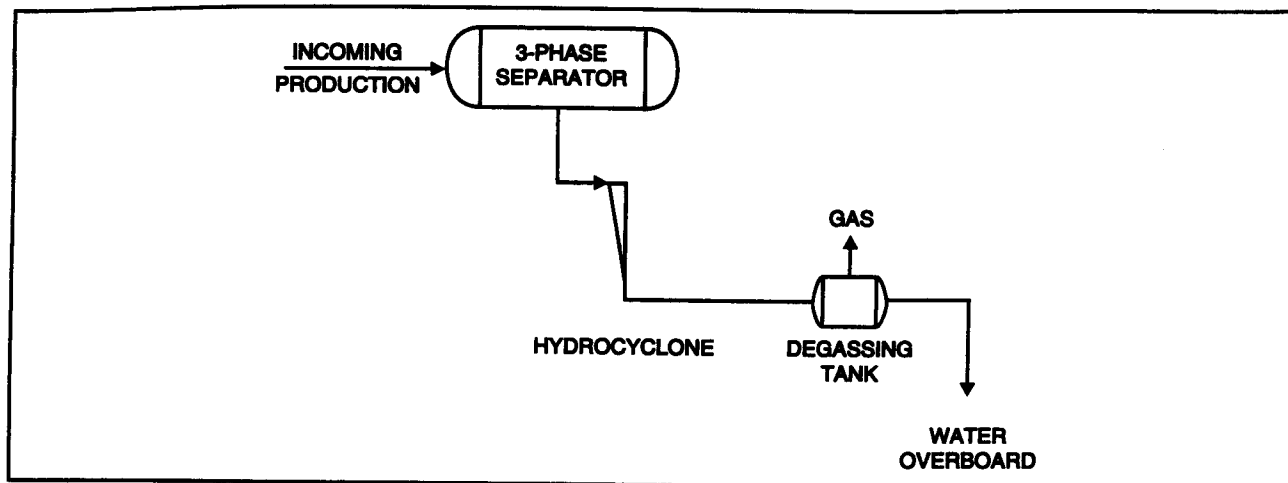


Figure 8.2 Offshore Produced Water Treatment with a Hydrocyclone

Each of these pieces of equipment is described in Chapter 6 under the heading of Dispersed Oil Removal.

Centrifuges have been used to a limited degree, but are very costly. Membrane filtration has been tested, but presents significant operational challenges.

OIL-IN-WATER ANALYSIS

The oil content of a water depends on how it is measured. There is no absolute value.

Produced water contains both dispersed oil and “dissolved oil”. The dissolved oil consists of hydrocarbons, phenols, organic acids, and low molecular weight aromatic compounds such as benzene and toluene.

Normal oil/water separation equipment cannot remove dissolved organic compounds. However, values of “oil and grease” include *both* the dispersed oil and some of the dissolved organic compounds. *Hence, equipment performance cannot be accurately evaluated using “oil and grease” values.*

A description of the various ways of measuring the oil content of a produced water are given in Chapter 2.

TOXICITY ISSUES

The United States Environmental Protection Agency began requiring biomonitoring of aquatic toxicity for produced water discharges in the Outer Continental Shelf of the Gulf of Mexico in December, 1993.

Aquatic toxicity is measured by comparing survival, growth and fecundity (egg production) of living organisms in either synthetic water or natural seawater with that of the same type of organism exposed to that same water containing varying percentages of produced water.

Toxicant Identification

Toxic effects resulting from the discharge of produced water is the result of naturally occurring toxic components originating from contact with the produced hydrocarbons and/or the formation rock and/or treatment chemicals, which end up in the water phase.

The identity of the most likely toxicants has not been established with certainty. However, some of the more likely culprits are summarized in the following section.

Treating Chemicals

It can be determined if treatment chemicals are the primary cause of toxicity by measuring the toxicity of the produced water prior to chemical addition, and again after chemicals have been added. If treatment chemicals prove to be the source of the problem, the identity of the specific chemical or chemicals responsible can be established through a series of toxicity tests using the produced water and different combinations of treatment chemicals.

Treating chemicals can be classified in three categories:

1. Production Treating Chemicals

- | | | |
|------------------------|----------------------|----------------------------|
| • Emulsion Breakers | • Paraffin Compounds | • Water Treating Chemicals |
| • Detergents/Cleaners | • Biocides | Coagulants |
| • Corrosion Inhibitors | • Scale Inhibitors | Flocculants |
| • Oxygen Scavengers | • Antifoamers | Reverse Breakers |

2. Gas Processing Chemicals

Typically methanol and/or glycol for hydrate inhibition, or glycol for gas dehydration.

3. Stimulation And Workover Chemicals

Production treating chemicals are the largest single source of concern, because these chemicals come in contact with produced water.

The Most Toxic?

The following types of compounds appear to offer the greatest potential for toxicity based on acute toxicity data using varying species and protocols:^(8.2)

1. Quaternary Ammonium Compounds

“Quats” as they are often called, are commonly used as biocides, corrosion inhibitors, reverse breakers, and coagulants. They are quite soluble in water.

2. Amine Salts

Amines are commonly used as corrosion inhibitors and biocides.

Chemical Treatment Issues

1. System Application

Chemicals injected into pipelines or water injection systems will not be discharged overboard, and so are not of concern. Glycol dehydration of gas is performed in a closed system. Workover and stimulation chemicals can be caught and reused or treated prior to discharge.

The primary concern is treating chemicals which are added to the produced fluids and end up in the water phase.

2. Treatment Method: Batch or Continuous

Of particular interest are chemicals which are typically applied in high concentration batches in normal production operations. These include scale inhibitors (squeezes), corrosion inhibitors and biocides. Low level continuous treatment obviously offers a lower potential for toxicity.

3. Concentration

One must consider three concentrations: The actual treatment concentration, the concentration of the chemical in the water when it is discharged overboard, and the No Observable Effect Concentration (NOEC).

Some fraction of the chemical injected into the system will be consumed or retained in the system, which reduces the discharge concentration to a value less than the treatment concentration. In addition, if batch treatments can be staggered, the concentration of a chemical in produced fluids from one well will be diluted by production from other wells on the platform.

4. Solubility

Biocides and scale inhibitors are the two classes of chemicals which are highly soluble in water, as are water treatment chemicals such as reverse breakers, coagulants and surfactants. Corrosion inhibitors can be water soluble or oil soluble. Emulsion breakers typically have very little solubility in water, and most paraffin treating compounds tend to be more soluble in oil than in water.^(8.2)

Many treating chemicals contain multiple components, and one or more of these may be soluble in water, while others are not. There is also the question of how a particular component partitions between oil and water.

5. Adsorption

Chemicals which are not very soluble in water can adsorb on the surface of solids, such as corrosion products, which can end up in the water being discharged overboard.

Naturally Occurring Toxicants

If toxicity proves to be the result of chemical compounds which are naturally present in the produced water, the cause of the toxicity is typically identified by subdividing the water into various fractions and experimentally determining the toxicity of each fraction. A series of fractionation procedures, each designed to remove a class of compounds, is used to subdivide the mixture into a number of samples that can be tested individually. This procedure makes it possible to identify the class of compounds responsible for the toxicity.

The primary naturally occurring toxicants found in produced waters are:

- | | |
|---|-----------------|
| • Dispersed Oil | • Radionuclides |
| • Soluble Oil | • Sulfides |
| • Heavy Metals:
Cd, Cr, Cu, Pb, Ni, Ag, Zn | • Ammonia |

In addition, many produced waters have extremely high salinities, and all produced waters are essentially free of dissolved oxygen.

While identification of most naturally occurring toxicants is reasonably straight forward, the definition of soluble oil is somewhat more elusive. The term "soluble oil" is often used to describe the organic materials which are dissolved in the water. Rabalais^(8.3) categorized them in four groups in descending order of abundance:

1. Organic Acids: The largest component.

Fatty Acids: Water produced with paraffinic oils often has high concentrations of fatty acids. However, the fatty acids in produced water are produced as sodium salts of the acid.^(8.4)

Aromatic Acids: Water produced with asphaltic oils contains notable amounts of naphthenic acids.

2. Saturated Hydrocarbons
3. Volatile Aromatics and Phenols: Benzene and toluene comprise about 80% of these compounds. They are typically more abundant in produced waters from gas condensate operations.
4. Polynuclear Aromatics: Smallest fraction; however, it is also the most toxic.

Toxicity Reduction

If you wish to reduce the toxicity of a given discharge, it is necessary to first identify the cause(s) of the toxicity.

Treatment Chemicals

If toxicity is due to treatment chemicals, there are several options which might result in reduced toxicity:

1. Chemical Substitution

The first option would be to substitute a less toxic treatment chemical for the offending product. For example, a glutaraldehyde might be substituted for a quaternary amine biocide.

2. Change Treatment Method

The use of continuous treatment in place of batch treatment would substantially reduce peak chemical concentrations in the produced fluids. This could significantly reduce toxicity.

3. Alter Chemical Composition

The use of a less toxic solvent package, or alteration of the solubility characteristics to reduce the concentration in the water phase could reduce toxicity.

Natural Toxicity

Reduction of naturally occurring toxicity is somewhat more problematic due to the cost of additional equipment, increased operating costs, and space and weight limitations on offshore platforms.

Some of the more common water treatment equipment which could be considered for the purpose of reducing naturally occurring toxicity are:

1. Gas Flotation

Dispersed gas flotation cells are commonly used offshore to reduce the oil and grease levels in produced water to acceptable levels. A flotation cell can also tend to lower the concentration of suspended solids.

2. Hydrocyclones

Hydrocyclones are commonly used to reduced the concentration of dispersed oil in produced water. This type of equipment typically has little effect on suspended solids.

3. pH Adjustment

Modest pH adjustment using phosphorous acid has been successfully employed in the Gulf of Mexico as a means of precipitating "dissolved oil" so that it can be removed with dispersed gas flotation.

4. Filtration

Filtration equipment is primarily used to reduce the concentration of suspended solids in produced water. However, it is also used to reduce the concentration of dispersed oil.

5. Air Stripping

Air stripping using a countercurrent stripping tower(s) could be used to reduce the concentration of volatile fractions. Of course, the impact on air quality would have to be considered, and some sort of scrubber would probably be required.

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WATER TREATMENT FOR ENHANCED OIL RECOVERY

Oil recovery mechanisms for petroleum reservoirs can be categorized as shown in Figure 9.1.

Those mechanisms listed under "Secondary Recovery" are usually referred to as "Enhanced Oil Recovery" techniques, or simply EOR.

The EOR processes which use water are listed in Table 9.1 along with an estimate of the required water volumes.

Note that the volume of water required for the EOR techniques listed is typically far greater than the volume of oil recovered. Proper treatment of the water for each process is of extreme importance.

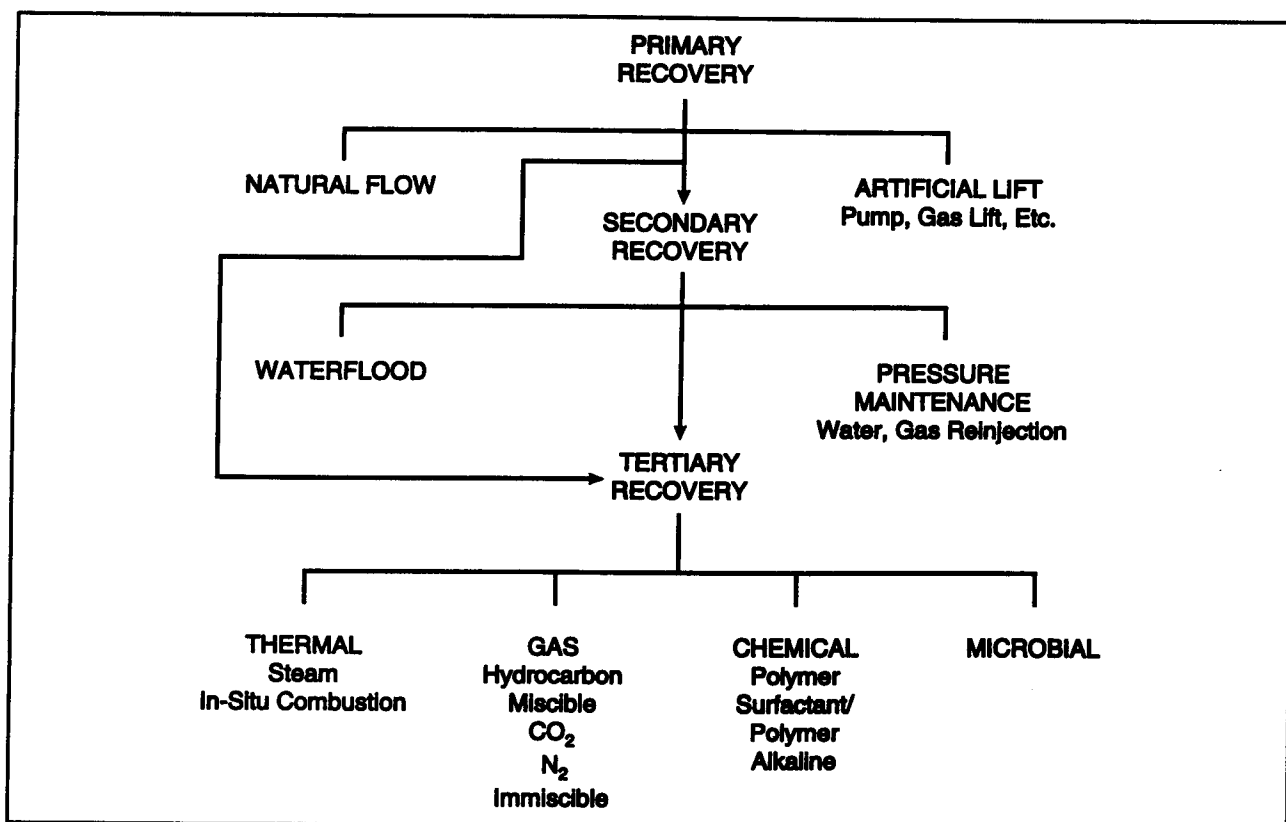


Figure 9.1 Oil Recovery Mechanisms^(9.1)

TABLE 9.1
Estimated Water Usage for EOR Processes^(9.2)

Process	Water Usage (bbl water/bbl oil)
Polymer	16-50
Surfactant — Polymer	10-15
Alkaline (Caustic)	22-33
Carbon Dioxide	1-3
In-situ Combustion (Wet)	0.5-1
Steam	2-5

POLYMER FLOODING

A polymer flood is carried out by injecting an aqueous polymer solution into the reservoir to displace the oil from the rock into producing wells. The polymer increases the viscosity of the solution which increases its ability to displace viscous crude oils. Other mechanisms are also involved, but they will not be discussed.

The composition and properties of the water which is used to make up the polymer solution are quite important, as they affect the viscosity of the solution. Also important are the agents which cause polymer degradation and decreases in solution viscosity, which can cause a reduction in displacement efficiency.

Two basic types of polymers are currently the most widely used: polysaccharides and polyacrylamides.

Polysaccharides

The polysaccharide typically used in enhanced oil recovery processes is xanthan gum and is often referred to as a "biopolymer." It has a molecular weight of about 5 million.

Xanthan gum is produced by the microbial action of *xanthomonas campestris* on a carbohydrate substrate. The biopolymer is an extracellular slime which forms on the surface of the bacterial cell. The fermentation broth is pasteurized to kill the *xanthomonas campestris*, and the polymer is precipitated from the broth by a suitable alcohol.^(9.3)

Xanthan gum solutions exhibit relatively stable viscosity properties as a function of salt concentration, pH, and temperature.^(9.4)

Microbiological Problems

Once a biopolymer is dissolved in water, it is highly susceptible to bacterial attack by both aerobic and anaerobic microorganisms, resulting in a significant reduction in solution viscosity.^(9.3,9.5) In addition, some aerobic slime forming bacteria produce biological masses which contribute significantly to formation plugging.^(9.3)

Water Salinity Effects

The viscosity of xanthan solutions increases with increasing brine salinity. The presence of multivalent cations has no additional effect on viscosity beyond their contribution to total salinity.^(9.6)

Dissolved Oxygen

At room temperature, dissolved oxygen has no apparent effect on the viscosity of biopolymer solutions. However, at higher temperatures, enormous losses in viscosity are observed. ^(9.7)

pH Effects

The maximum fresh water solution viscosity has been observed at a pH of 5.5. Polymer viscosity is highest in high or low pH solutions. ^(9.8)

Polyacrylamide

The polyacrylamide molecule is a long chain made up of acrylamide monomer molecules. It has a basic structure as follows:

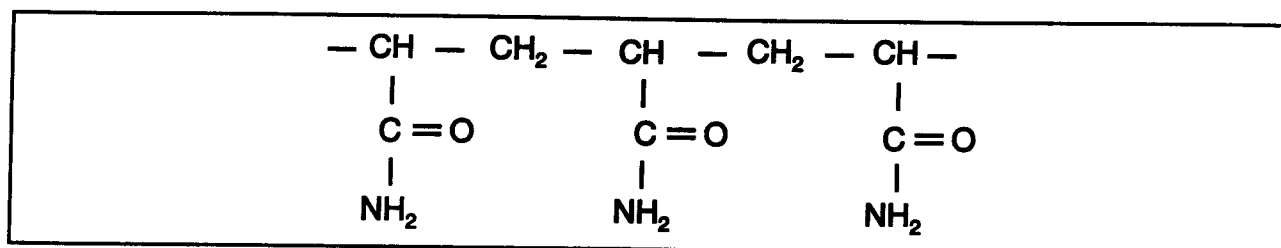


Figure 9.2 Basic Structure of Polyacrylamide

There are several mechanisms involved in the formation of the polymer molecule, which results in a wide range of chain lengths. The average molecular weight of commercial polyacrylamides typically ranges from 1 to 10 million.

Polyacrylamide is usually modified by chemically replacing some of the amide groups with carboxyl groups. This process is called hydrolysis, and the percentage of amide groups which have been replaced by carboxyl groups is referred to as the percent hydrolysis. The percent hydrolysis typically ranges from 0 to 30%. The primary reason for carrying out partial hydrolysis is to increase the viscosity of the polymer solution. The apparent solution viscosity of a partially hydrolyzed polyacrylamide dissolved in fresh water is much greater than that of a corresponding unhydrolyzed polyacrylamide. ^(9.3)

The carboxyl group ionizes in water, leaving a negative charge. The net result is a series of negative charges along the polymer chain, creating a negatively charged polymer. ^(9.9) This type of polymer is often referred to as an anionic polyelectrolyte.

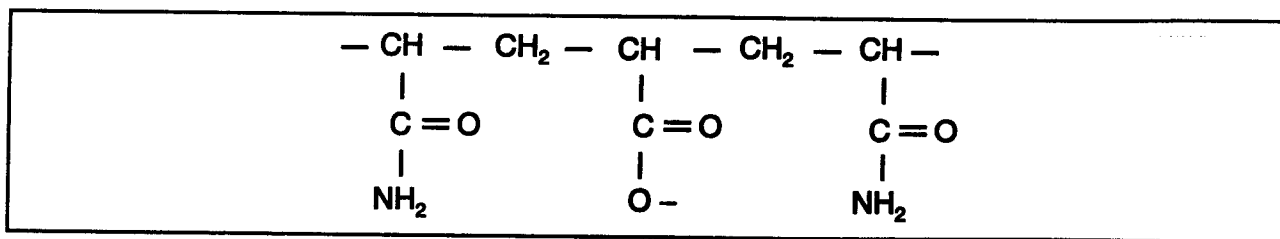


Figure 9.3 Partially Hydrolyzed Polyacrylamide

Polyacrylamides can be manufactured in the field using small portable plants.

Effect of Sodium, Calcium and Magnesium Ions

Increasing concentrations of sodium ions result in decreased viscosity of partially hydrolyzed polyacrylamide solutions. This is illustrated for a 0.25% solution of partially hydrolyzed polyacrylamide in Figure 9.4.

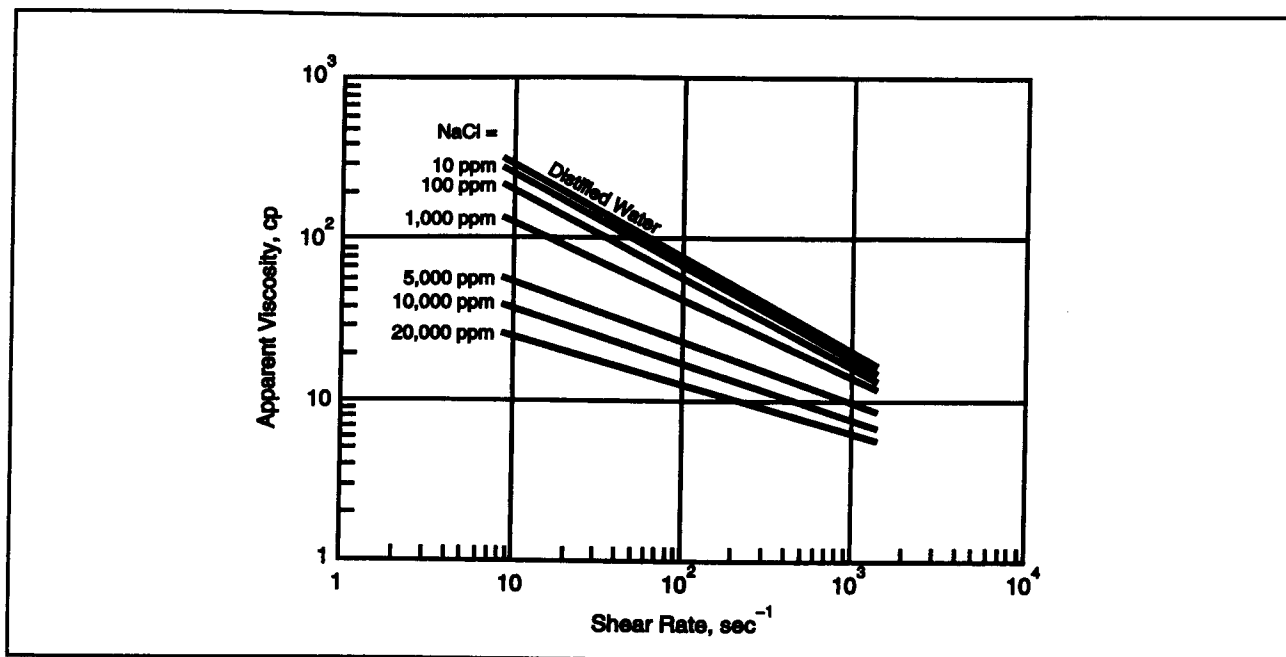


Figure 9.4 Effect of NaCl Concentration on Polymer Solution Viscosity^(9.9)

This occurs because of neutralization of the electrical charges within the polymer molecules by the oppositely charged sodium ion. As the net charge on the polymer molecules decreases, the repel-lent force between molecules diminishes. The polymer chains coil up into a ball, thus causing a decrease in solution viscosity.^(9.9,9.10,9.11)

Both calcium and magnesium ions cause larger decreases in viscosity than sodium ions.^(9.9) Calcium ions cause a greater reduction in viscosity than an equivalent amount of magnesium ions, and mixtures of calcium and magnesium ions cause even greater reductions than either ion alone. The effect of salts on the viscosity of a 2500 ppm solution of partially hydrolyzed polyacrylamide is shown in Figure 9.5.

Effect of Oxygen

The presence of dissolved oxygen has a number of negative effects. It can cause:

- Dramatic increases in the corrosion rate of any carbon steel in the system.
- Precipitation of dissolved iron.
- Support the growth of aerobic microorganisms.
- Significant polymer degradation. Partially hydrolyzed polyacrylamides are very sensitive to oxidation, especially in higher temperature reservoirs.^(9.9,9.12)

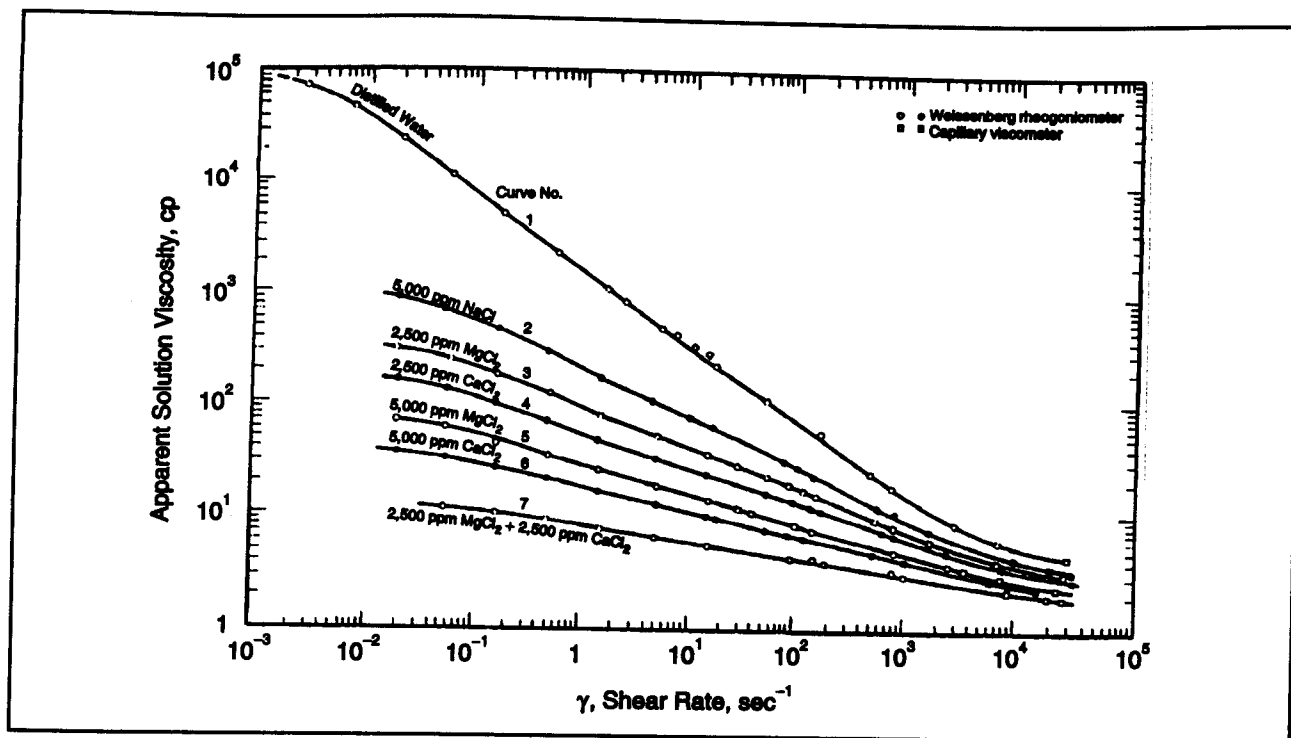


Figure 9.5 Effect of Salts of the Viscosity of a Polymer Solution

Microbiological Problems

Polyacrylamides are relatively immune to bacterial attack.^(9.3) However, the presence of aerobic microorganisms can contribute significantly to corrosion and plugging problems, and sulfate reducing bacteria have been observed as a contributor to corrosion problems in polymer injection systems.^(9.13)

pH Effects

Lowering the pH of the polymer solution by adding a small amount of acid lowers the viscosity of the solution. Acid exerts a greater influence on the shape of the molecules than an equivalent amount of a neutral salt. The hydrogen ions convert the ionic carboxylate groups in the molecules to uncharged carboxylic acid groups.^(9.10)

Effect of Oxygen Entry

If oxygen is excluded, the presence of dissolved iron ions appears to have only a slight effect on solution viscosity. However, if oxygen entry is permitted, a rapid decline in viscosity occurs.^(9.14)

Oxygen entry also results in the precipitation of iron ions from solution as insoluble ferric hydroxide. It is an excellent plugging agent by itself, but in the presence of high molecular weight polymers, the problem is considerably more severe.

Water Treatment for Polymer Flooding

The water used to make up polymer solutions should be as clean as possible.

Polymers tend to adhere to solids and agglomerate. When produced water is used, oil carryover is not generally considered an acute problem, but should be minimized because of relative permeability considerations and the fact that oil also helps to agglomerate solids and aggravate plugging.

Filtration and Oil Removal

Filtration is frequently necessary, and dispersed oil removal is nearly always necessary when produced waters are used.

Permissible levels of suspended solids and oil are subject to discussion. One prominent chemical supplier advocates 1 ppm suspended solids and 1 ppm oil.^(9.15) A major oil producer in West Texas quotes polymer supplier recommendations that the water should have less than 20 ppm of hydrocarbons, and no solid particles over 2 microns.^(9.16)

It may also be necessary to filter the polymer solution to remove any gelled agglomeration of high concentration polymer that might result in injection well plugging.

Corrosion

Plastic piping and plastic or coated steel vessels and equipment should be used to prevent corrosion and the generation of iron compounds.

Bacterial Control

The water should normally be treated with a biocide prior to mixing with the polymer.^(9.13) Laboratory testing should be conducted to ensure that the biocide will not degrade the polymer.^(9.17)

The use of an effective biocide is absolutely essential for polysaccharide polymer solutions and is strongly recommended for polyacrylamide solutions.

Dissolved oxygen should be excluded to prevent the growth of aerobic bacteria.

Dissolved Oxygen Removal

Oxygen must be excluded or removed from polyacrylamide solutions to prevent degradation. It is best to eliminate all oxygen before the polymer is added, and then add the polymer in such a way that oxygen is not introduced. This minimizes the need for oxygen scavengers in the polymer solution.

Oxygen exclusion is also recommended for polysaccharide polymer solutions, although degradation only occurs in high temperature applications.

Oxygen also accelerates the corrosion of carbon steel, causes the precipitation of soluble iron from solution, and facilitates the growth of aerobic bacteria.

The use of *oxygen scavengers* in polymer solutions presents a number of unusual problems, and they must be used with care. It is usually best to remove dissolved oxygen from the water before the polymer is added, and then try to prevent air entry during polymer mixing.

One of the problems with the use of conventional sulfite oxygen scavengers is that, given a choice between reacting with sulfite and ferrous ions, oxygen will first oxidize the ferrous iron to insoluble ferric iron. However, oxygen reacts with sodium hydrosulfite in preference to the ferrous ion.

In addition, it is such a powerful reducing agent that it is able to re-solubilize ferric hydroxide which has already formed in the system.

For this reason, many early polyacrylamide polymer floods used sodium hydrosulfite (sodium dithionate) as an oxygen scavenger.^(9.13) The problem with this material is that while stable in powder form, it deteriorates within a few hours when dissolved in water.^(9.17)

Because of the difficulties in applying a powdered product in the field, it is more common to control the ferrous iron content of the water and use sodium or ammonium bisulfite oxygen scavengers. The problem in their use arises from the fact that they usually must be catalyzed with divalent metal ions, which can contribute to polymer degradation.^(9.17)

Although dissolved oxygen does not cause degradation of polysaccharides at normal ambient temperatures, it does result in serious degradation at elevated temperatures. Unfortunately, neither sulfite or sodium hydrosulfite oxygen scavengers can be used to remove dissolved oxygen from polysaccharide polymer solutions, because they produce free radicals as intermediate products that can initiate biopolymer degradation. Thus oxygen removal prior to mixing is necessary. The use of antioxidants may also be required.^(9.7)

All vessels should be blanketed with nitrogen.

Iron

Many waters contain very small amounts of natural iron. When this is the case, oxygen exclusion and the use of plastic piping, and plastic or coated steel vessels and equipment to prevent the generation of iron due to corrosion, will minimize any problems due to iron.

If high iron levels are naturally present, dissolved iron removal and oxygen exclusion will be necessary.

Scale Control

The scaling tendencies of all waters should be evaluated. Because the pH of polymer solutions is frequently basic, calcium carbonate scale may be a problem. Scale inhibitors must be selected which are compatible with the polymer.

Sodium, Calcium and Magnesium Ions

Since the viscosity of polysaccharide polymer solutions increases with increasing salinity, it may be desirable to increase the salinity of the water when using biopolymers.

The presence of sodium, calcium and magnesium ions has the opposite effect on partially hydrolyzed polyacrylamide solutions, and their concentrations must be limited for maximum viscosity increase. For that reason fresh waters are normally used where available. Softening may be employed to remove calcium and magnesium ions if desired.

In many cases, however, brines are used with polyacrylamides and the negative effects of these ions are ignored if a sufficient increase in viscosity can be achieved to materially increase oil recovery.

SURFACTANT-POLYMER FLOODING

In this process, oil is displaced from the reservoir rock as shown in Figure 9.6.

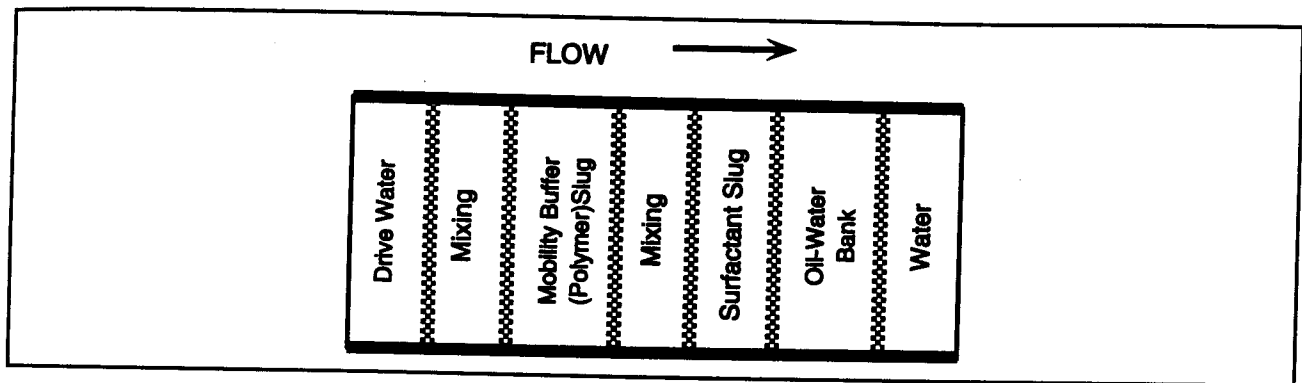


Figure 9.6 Schematic Diagram of the Surfactant-Polymer Process

In most cases, the surfactant slug ahead of the polymer is a micellar solution, sometimes referred to in the literature as a microemulsion, soluble oils, or swollen micelles.^(9.1) Its primary purpose is to lower the interfacial tension and miscibly displace oil that cannot be displaced by water.

Micellar solutions contain at least three components: hydrocarbon, surfactant, and water. The hydrocarbon can have a broad range of compositions, and the surfactant is usually a petroleum sulfonate. The water must be fresh.

Alcohol can be added as a fourth component. It serves as a co-surfactant and increases the latitude in the composition of micellar solutions.

If distilled or deionized water is used, salts may be added. They tend to lower the viscosity of the micellar solution and increase phase stability.^(9.18)

Additives such as biocides may be incorporated into the micellar solution.

Surfactant slugs with compositions other than micellar solutions are also used.^(9.13)

Water Treatment

Exceptionally clean water of carefully controlled composition is used to make up the surfactant slug. Requirements vary with the specific surfactants used.

CAUSTIC OR ALKALINE FLOODING

When crude oil is displaced by water, the displacement efficiency can be improved by lowering the interfacial tension between the two fluids. In many cases this can be accomplished by the addition of a strong base to water. Sodium hydroxide (caustic) and sodium orthosilicate have been widely used due to cost considerations.

At typical use concentrations, the pH of the alkaline solution is in the range of 12 to 13.

Effect of Divalent Ions

At these very high pH values, the precipitation of divalent ions such as calcium, magnesium and iron as hydroxides can be anticipated. Hence, these ions must not be present, and softening is normally required to reduce the total hardness of the water used to make up the alkaline solution to less than 1 mg/L as CaCO_3 .^(9.19)

Effect of Salinity

It usually requires a lower concentration of caustic or sodium orthosilicate to achieve the required interfacial tension when some NaCl is present.^(9.19) The required level is established experimentally for the specific crude oil in question.

Water Treatment

Suspended solids and dispersed oil must be removed. Additional water treatment usually consists of adjustment of salinity to the desired value by the addition of NaCl, or by blending with another water, followed by softening to remove the divalent metal ions.

CARBON DIOXIDE INJECTION

When carbon dioxide mixes with crude oil, under certain conditions a single-phase fluid is formed which is miscible with the reservoir oil. The objective of CO_2 injection is to form a miscible bank to displace the oil, and then to displace the miscible bank with gas or water.

Of the several methods of CO_2 injection, three also utilize water injection:^(9.20)

- Injection of a slug of CO_2 followed by water.
- Alternate injection of slugs of CO_2 and water. Also known as the WAG process.
- Simultaneous injection of CO_2 and water.

Water Treatment

The water which is injected is usually produced water, and it should be processed in exactly the same way it would be for normal water injection.

Corrosion Control

The only additional problem is the increased corrosiveness when the water and carbon dioxide mix. Mixing occurs only once in the first process: at the interface between the CO_2 and water. The effect of the increased corrosion rates during this period on the overall life of the system should be minimal.

In the WAG process water and CO_2 are transported to the injection wells through separate lines. Mixing of the two fluids occurs in the injection wells at the end of each cycle, and can result in severe corrosion.^(9.20)

Simultaneous injection of the two fluids presents the largest amount of mixing of the two fluids, as well as the most severe corrosion problems.

The primary methods of corrosion control in the areas where mixing occurs are corrosion resistant materials (both metallic and non-metallic), coatings and linings.^(9.20)

IN-SITU COMBUSTION

In-situ combustion involves the injection of air or oxygen into the reservoir. Spontaneous ignition occurs in the vast majority of reservoirs, and the combustion zone moves away from the injection well consuming part of the reservoir oil as fuel. The result is an extremely complex displacement process, as shown in Figure 9.7.

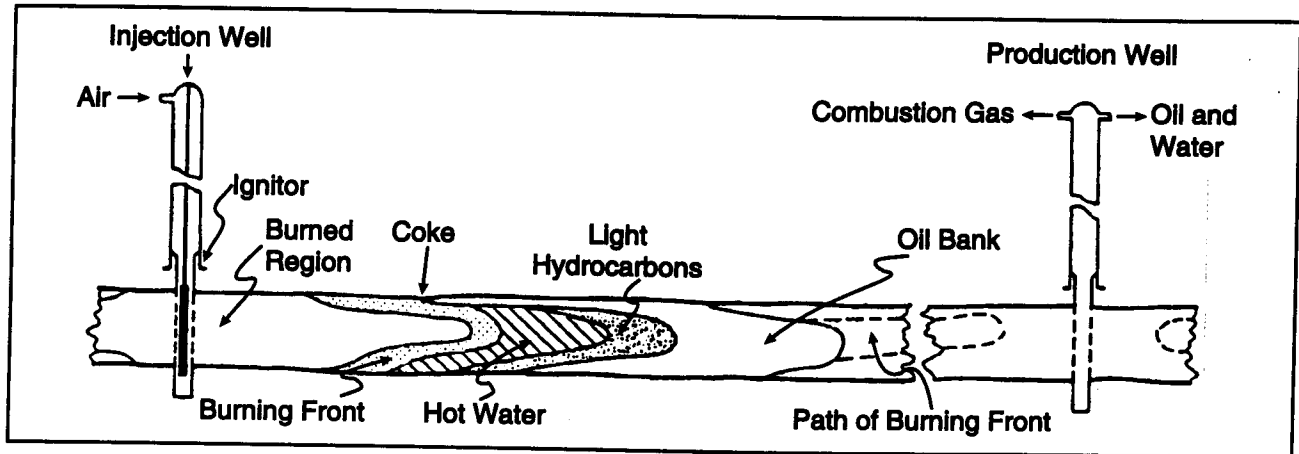


Figure 9.7 Forward In-Situ Combustion Process^(9.3)

Water may also be injected along with the air. This process is referred to as a Combination of Forward Combustion and Waterflooding (COFCAW). The water is heated by the residual heat in the rock behind the combustion zone, flashes into superheated steam and enhances the oil displacement process. However, the major benefit of simultaneous water injection is a reduction in the amount of air required to recover a barrel of oil by a factor of three or more.^(9.21)

The water and air are normally kept separate by injecting one fluid down the tubing and the other down the annulus in order to minimize oxygen corrosion. A joint of Inconel tubing on the bottom of the tubing string will effectively control corrosion in the area of mixing.^(9.22)

There seems to be no special requirement for water used in the COFCAW process other than it should be of good quality to avoid downhole plugging problems.^(9.22) Hence, normal treatment procedures should be adequate.

STEAM INJECTION

Although listed last, steamflooding is by far the major enhanced recovery process at present. An Oil and Gas Journal survey of enhanced recovery projects published in April, 1984, concluded that over 75% of all enhanced production came from steam projects.^(9.1)

The purpose of injecting steam into a reservoir is to heat the crude oil and reduce its viscosity. Since the flow rate of oil through a reservoir rock is inversely proportional to its viscosity, considerable increases in production rates can be achieved.

There are two steam recovery techniques:^(9.3)

- **Steam Stimulation**

Sometimes known as cyclic steam injection, steam soak, or huff and puff. Steam is into a producing well for a period of several weeks. Steam injection is halted, the well is shut-in for a few days, and then placed on production. This cycle is then repeated as many times as desired.

- **Steamflooding**

Steamflooding is similar to waterflooding in that steam is injected into a number of injection wells and oil is produced from adjacent producing wells in a pattern. It is the principal steam injection method.

In either case, the injected steam is produced by a boiler which is usually referred to as a steam generator in oilfield operations. It is a once-through system which converts water to a mixture of approximately 80 percent steam and 20 percent water, normally referred to as 80% quality steam.

The steam generator feedwater must be treated to prevent corrosion and/or scale formation on the boiler tubes, as well as to prevent corrosion and the formation of scales or precipitates in the water phase. It should be noted that all of the dissolved solids in the feedwater will be concentrated in the water phase, which is injected along with the steam.

Corrosion Control

If the feedwater contains dissolved oxygen, it must be removed. This prevents boiler tube corrosion as well as the precipitation of soluble iron ions as iron hydroxide. Otherwise, no treatment is required.

The feedwater supply system should be constructed from non-metallic materials, or coated or lined steel. This prevents corrosion and the generation of iron.

Scale Control

All steam generator feedwaters must be softened to remove calcium and magnesium ions and prevent scale. The softened water should contain zero hardness (Total Hardness < 1 mg/L as CaCO_3).

Waters with less than 5000 mg/L TDS are softened using sodium ion exchangers. This process uses a strong-acid resin which is regenerated with a NaCl solution.

In order to achieve zero hardness with waters containing more than 5000 mg/L TDS, it is necessary to use weak-acid resins. Regeneration requires an acid followed by a base (usually HCl and NaOH).^(9.23)

Resin Fouling

Steam generator feedwater entering the ion exchange units must be quite clean. Dispersed oil, suspended solids, and precipitated iron compounds must be eliminated. Otherwise the resin will become fouled and its capacity for ion exchange will be reduced.

Other Precipitates

There is always a possibility of the formation of silica or sodium salt deposits when high TDS waters are used. However, this is usually controlled by limiting steam quality.^(9,23)

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NOTES:

10

COOLING WATER TREATMENT

Cooling water is circulated through equipment to absorb and carry away heat. The three basic types of cooling water systems are shown in Figure 10.1.

The open recirculating cooling water system is by far the most common and is the type used in most gas processing plants to cool compressed gas and overhead streams from fractionating towers.

Closed recirculating systems usually involve much smaller volumes of water and are often used to cool natural gas engine jackets and compressor cylinders.

Once-through cooling systems are seldom used because of the large volumes of water required and potential pollution problems when the water is discharged back to the environment.

OPEN RECIRCULATING COOLING SYSTEMS

In open recirculating cooling systems, the cooling water is pumped through a heat exchanger where the process stream is cooled and the water is heated. The warm water then passes to a cooling tower or spray basin where it is cooled by contact with air before circulation back to the heat exchanger.

The water is cooled in the tower or spray pond by evaporation of a portion of the circulating water. This evaporation loss results in an increase in the concentration of the dissolved solids in the circulating water since the evaporated water contains no dissolved solids. The water lost by evaporation must be replaced by makeup water.

Water is also lost by entrainment of droplets in the circulating air. This is called drift or windage loss. These droplets of circulating water contain the same concentration of dissolved solids as the rest of the circulating water. Therefore, their loss does not contribute to the concentration of dissolved solids in the system as does evaporation loss. However, windage losses must also be replaced by makeup water.

Water lost by inadvertent leakage must also be replaced.

Evaporation Losses

It requires approximately 1000 Btu's to evaporate one pound of water. This is equal to the amount of heat required to raise the temperature of 100 pounds of water 10°F [5.5°C]. Therefore, for

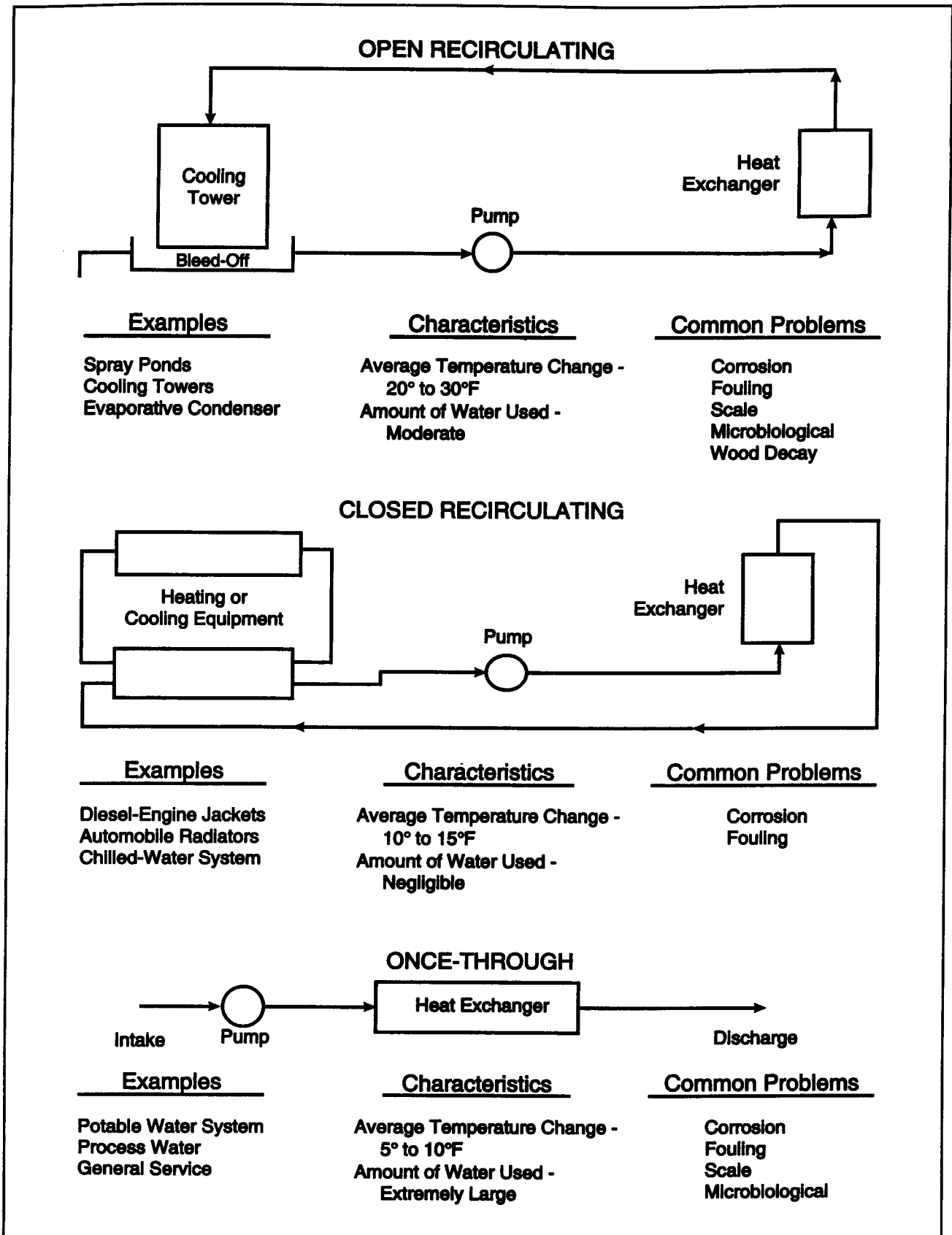


Figure 10.1 Cooling System Characteristics

each drop of 10°F [5.5°C] through the tower, one pound of water will be lost by evaporation per 100 pounds of water cooled. This is the equivalent of 1% of the water circulating. Therefore, the evaporation rate can be calculated as follows:

$$\text{Evaporation Rate (gpm)} = \frac{\text{Temperature Drop (° F)}}{10} \times \frac{\text{Circulation Rate (gpm)}}{100} \quad (10.1)$$

Windage Loss

Windage loss for *induced draft* cooling towers may be estimated as from 0.10 to 0.20 percent of water circulation. Reference to the cooling tower manufacturer's specification sheet will often establish this figure for the installation in question. Where 0.2 percent is guaranteed, use 0.15 percent, and where 0.1 percent is guaranteed, use 0.07 percent.

A much wider variation (0.3 to 1.0 percent) in windage losses occurs in *natural draft* towers, and most calculations can be based on total mechanical loss; i.e., blowdown plus windage. Windage loss in *spray pond* systems is typically 1 to 5 percent of the circulation rate.

Blowdown

Blowdown is the continuous or intermittent removal of some of the circulating water.

Evaporation results in increased concentration of the dissolved solids in the circulating water. The concentration is decreased by removing a portion of the circulating water and replacing it with makeup water containing a lower concentration of dissolved solids. Thus, the circulating water is diluted to control the buildup of dissolved solids in the circulating water.

Cycles Of Concentration

Cycles of concentration, or concentration ratio, is an expression of the degree to which the dissolved solids concentration in the original circulating water has been increased or concentrated by evaporation losses. Since the water originally introduced into the circulating system was "makeup water," the degree of concentration, or cycles of concentration, can be expressed as follows.^(10.1)

$$\text{Cycles} = \frac{\text{ppm chlorides in circulating water}}{\text{ppm chloride in makeup water}} \quad (10.2)$$

The chloride ion is normally used because it is quite soluble and seldom lost from water by precipitation.

Makeup Water

The amount of makeup water required is equal to the sum of all losses of water from the circulating system.

$$\text{Makeup} = \text{Blowdown} + \text{Windage} + \text{Evaporation} \quad (10.3)$$

Material Balance Calculations

In previous sections we have defined evaporation and windage losses, blowdown, cycles of concentration, and makeup. It is now possible to derive an equation for the calculation of blowdown rate by making a material balance based on chloride ion concentrations.

At equilibrium, the chlorides entering the system must equal the chlorides leaving the system. Furthermore, the chloride concentration in the blowdown is the same as in the circulating water.

Consider the following four equations:

$$M \times Cl_M = (B + W) \times Cl_B \quad (10.4)$$

$$Cl_B = Cl_R \quad (10.5)$$

$$M = B + W + E \quad (10.6)$$

$$C = \frac{Cl_R}{Cl_M} \quad (10.7)$$

Where:

- R = Circulation rate
- B = Blowdown rate
- M = Makeup rate
- W = Windage rate
- E = Evaporation rate
- C = Cycles of concentration

Substituting Equations 10.4 and 10.5 into Equation 10.3, we obtain:

$$(B + W + E) \times Cl_M = (B + M) \times Cl_R$$

Rearranging this expression into the form of Equation 10.6:

$$C = \frac{Cl_R}{Cl_M} = \frac{B + W + E}{B + W} \quad (10.8)$$

Equation 10.7 can be rearranged and solved for B to yield the following expression:

$$B = \frac{E - [W \times (C - 1)]}{C - 1} \quad (10.9)$$

Example 10.1: Given:

Circulation Rate	=	10 000 gpm
Water to tower	=	100°F
Water from tower	=	80°F
Guaranteed maximum windage loss	=	0.2%
Chlorides in tower makeup	=	100 ppm
Chlorides in circulating water	=	500 ppm

Example 10.1 (Cont'd.):

Determine:

1. Windage loss rate
2. Evaporation rate
3. Cycles of concentration
4. Blowdown rate
5. Total makeup rate

Solution:

$$1. \quad W = 0.0015 \times 10000 \text{ gpm} = 15 \text{ gpm}$$

(Assumes that actual losses were only 75% of the guaranteed maximum.)

$$2. \quad E = \frac{\Delta T}{10} \times \frac{R}{100} = \frac{100 - 80}{10} \times \frac{10000}{100} = 200 \text{ gpm}$$

$$3. \quad C = \frac{Cl_R}{Cl_M} = \frac{500}{100} = 5$$

$$4. \quad B = \frac{E - [W \times (C - 1)]}{C - 1} = \frac{200 - [15 \times (5 - 1)]}{5 - 1} = 35 \text{ gpm}$$

$$5. \quad M = B + W + E = 35 + 15 + 200 = 250 \text{ gpm}$$

COOLING WATER TREATMENT OBJECTIVES

Cooling waters are treated to prevent four types of problems:

1. Scale formation on the heat transfer surfaces.
2. Corrosion of metal piping and heat exchangers by the cooling waters.
3. Fouling of the heat exchangers and the cooling tower.
4. Deterioration of wooden cooling towers.

Scale Prevention

Calcium Carbonate Scale

Calcium carbonate scale is extremely common in cooling waters, especially in the heat exchangers where the water is hottest.

The Ryznar Index

The Ryznar Stability Index is commonly used to estimate calcium carbonate scaling tendencies for cooling waters. It should be calculated for both the makeup water and the circulating water. The most common methods of preventing calcium carbonate scale are:

1. If the makeup water is not scaling, control the number of cycles of concentration so that the Ryznar Stability Index will not exceed 6.0.

2. Add sufficient acid to the makeup water to maintain the pH of the circulating water at a value slightly less than pHs.

Sulfuric acid is normally used for pH control since it is usually the most economical. However, caution must be exercised not to precipitate calcium sulfate scale. This is most likely to occur when the makeup water is high in sulfates and alkalinity.

The rule of thumb for avoiding calcium sulfate scale is to limit the concentration of calcium sulfate in the circulating water to a maximum of 1700 ppm. Another guide is that the calcium concentration multiplied by the sulfate concentration (when both are expressed in ppm) should not exceed 500 000.

If calcium sulfate scale becomes a problem, HCl can be substituted for H₂SO₄.

3. Use inorganic polyphosphates (sometimes in conjunction with pH control) or organic scale inhibitors.

Magnesium Scales

Magnesium hydroxide will precipitate only in very alkaline waters and is not a widespread problem. Magnesium carbonate is usually controlled in the same manner as calcium carbonate.

Silicates

Prevention of silicate scale deposition is normally achieved by limiting the silica concentration in the cooling water to a maximum value of 175 ppm (preferably 150 ppm).

The cycles of concentration based on the silica ratio should not be allowed to fall appreciably below the cycles based on chlorides and hardness, as this would indicate silica deposition. If both silica and magnesium cycle at a lower figure than chlorides, this indicates deposition of magnesium silicate.

Pretreatment of Makeup Water

The formation of calcium and magnesium scales can be prevented by removing the calcium and magnesium ions (hardness) and alkalinity from the water by a softening process. The cold lime process (see Chapter 6) is commonly used for cooling water.

Corrosion Control

Inorganic corrosion inhibitors such as chromates, polyphosphates, or a combination of the two, have been used for corrosion control for many years. Zinc is also used in combination with either chromates, polyphosphates, or both, to improve inhibition.

Since many of these materials are toxic to living organisms, disposal of blowdown into surface waters can pose a serious pollution hazard. In fact, chromates are seldom used because of disposal problems.

Organic inhibitors have generally been less effective in cooling waters than the inorganics.

Microbiological Control

Algae, fungi, and bacteria can all contribute to problems in open cooling water systems. They can encourage corrosion, cause fouling and cause deterioration of the wood in cooling towers.

Chlorine is most widely used to control the growth of microorganisms.^(10.2) A chlorine residual of 0.3 to 1.0 ppm is usually adequate. Chlorine residuals of greater than 1.0 ppm for long periods can cause deterioration of tower wood, and should be avoided.

A common procedure is to chlorinate to a residual of 1.0 ppm for four hours each day. Continuous chlorination to maintain a residual of 0.2-0.3 ppm is also used, but this may necessitate a periodic slug treatment with another biocide to kill resistant growths.

Fouling

Fouling of heat exchanger tubes and cooling towers is usually defined as the deposition of non-scale-forming materials such as:^(10.3)

1. Suspended solids in the makeup water
2. Particulate matter from the atmosphere
3. Biological masses
4. Corrosion products
5. Hydrocarbon contamination due to process leaks

Filtration and/or coagulation and settling may be employed to remove suspended solids from the makeup water. Side stream filtration and/or silt dispersants may be employed in the circulating system to reduce solids deposition. Biocides and corrosion inhibitors are used to prevent the generation of corrosion products and biological masses.

Tower Wood Deterioration

Tower wood deterioration can usually be avoided by following three rules:

1. Maintain an effective biocide treating program from start-up.
2. Avoid excessive chlorination. (1.0 ppm residual for long periods)
3. Maintain the pH of the water at less than 8.3.

CLOSED RECIRCULATING COOLING SYSTEMS

A closed recirculating cooling system is one in which the water is circulated in a closed loop. The heat absorbed in the cooling operation is dissipated in some type of heat exchanger. Air-fan coolers are frequently used.

Since the cooling system is closed, there is no evaporation, and therefore no change in water composition.

High chemical treatment levels are often required, but since water losses are negligible, these levels are economical. Excellent quality makeup water is generally used for best system operation.

The advantages of a closed system lie in improved control of cooling water temperature through the heat producing unit, and in the relative freedom from the problems of operating an open system.

REFERENCES

- 10.1 Ostroff, A. G.: *Introduction to Oilfield Water Technology*, Second Edition, National Association of Corrosion Engineers, Houston, Texas (1979).
- 10.2 Kemmer, Frank, N., Editor: *The Nalco Water Handbook*, McGraw Hill, New York (1979).
- 10.3 Betz: *Betz Handbook of Industrial Water Conditioning*, Seventh Edition, Betz Laboratories, Inc., Trevose, Pa. (1976).

11

BOILER WATER TREATMENT

Although there are many different types of boilers, they are all essentially devices for transforming liquid water to steam by heating the water. When the water evaporates, the dissolved solids are left behind and frequently form scales and deposits. Deposition on heat transfer surfaces can cause the metal to overheat, leading to premature failure.

Corrosion can also be a serious problem in boilers. Dissolved gases such as oxygen, carbon dioxide or hydrogen sulfide pass with the steam, causing corrosion of steam and condensate lines. Low pH values also contribute to corrosion.

Boilers are usually classified in terms of their operating pressure, but it is the corresponding operating temperature which dictates the degree of treatment required for boiler feedwaters. The higher the operating pressure (and temperature), the more stringent the treatment requirements.

An arbitrary classification of boilers is given in Table 11.1.

TABLE 11.1
Boiler Classification

Operating Pressure	Classification
Less than 200 psi	Low Pressure
200-500 psi	Intermediate Pressure
500-2000 psi	High Pressure

Most boilers used in the oilfield are of the low or intermediate class. The purpose of boiler feedwater treatment is threefold:^(11.1)

1. Prevent the formation of scales and deposits.
2. Minimize or prevent corrosion in the boiler and steam systems.
3. Maintain steam purity. The primary causes of decreased purity are carryover of water droplets, and silica dissolved in the steam.

Boiler feedwater treatment is classified as external or internal treatment. External treatment means that the water composition is altered before it enters the boiler. Typical external treatment processes include softening, demineralization, deaeration, iron and manganese removal, filtration, or some combination.

Internal treatment refers to chemicals added to the water which react inside the boiler to prevent scale, corrosion, or foaming.

EXTERNAL TREATMENT

Boiler feedwater should have the lowest hardness, alkalinity, sulfates, silica, and suspended solids levels that can be economically afforded.

Maximum permissible concentrations for each constituent in the feedwater cannot be set. However, a preliminary estimate can be made from the recommended boiler water composition limits published by the American Boiler Manufacturers Association (ABMA) as shown in Table 11.0.

TABLE 11.2
Recommended Maximum Limits in the Boiler

Boiler Pressure (psig)	Total Dissolved Solids (ppm)	Total Alkalinity (ppm)	Suspended Solids (ppm)	Silica (ppm)
0-300	3500	700	300	125
301-450	3000	600	250	90
451-600	2500	500	150	50
601-750	2000	400	100	35
751-900	1500	300	60	20
901-1000	1250	250	40	8
1001-1500	1000	200	20	2.5
1501-2000	750	150	10	1.0
Over 2000	500	100	5	0.5

*Silica limits based on limiting silica in steam to 0.02-0.03 ppm

Iron and oxygen in the feedwater should be near zero.

Continuous blowdown can be employed to limit the concentration of the various constituents in the boiler shell. However, if the feedwater composition is such that very high blowdown rates are required, then it is generally more economical to remove offending constituents by external treatment of the feedwater.

Three basic types of processes may be carried out in the external treatment of boiler feedwater:

1. Suspended solids removal
2. Dissolved gas removal
3. Water softening

These processes are discussed under the heading of Water Processing Technology.

INTERNAL CHEMICAL TREATMENT

Internal chemical treatment is usually necessary to provide insurance against scale and corrosion even if the water has been externally treated. When boilers are operated at low to moderate pressures, and the raw feedwater is of good quality (low hardness, silica, and turbidity), internal treatment alone will often be adequate.

Scale Control

Scale formation within a boiler is controlled by precipitation of calcium and magnesium as a non-adherent sludge, or by chelation of the calcium and magnesium ions.

Phosphate Treatment

A soluble sodium phosphate is added which reacts with calcium to form an insoluble precipitate, calcium phosphate. Magnesium and silica are precipitated as magnesium hydroxide, magnesium silicate, or calcium silicate. The alkalinity of the makeup is usually adequate to produce the necessary OH^- for the magnesium precipitation, although in some cases caustic must be added. The pH should be maintained above 9.5 both for magnesium precipitation and to ensure the formation of less adherent precipitates. A reserve or excess of 40 ppm $\text{PO}_4^{=}$ should be maintained.

Sludge dispersants may be used in conjunction with phosphates to prevent adherence of the precipitated particles and to maintain the resulting "sludge" as a non-adherent slurry. Sludge dispersants coat the finely divided particles as they are formed so that they will not form large crystalline precipitates. Smaller particles will remain dispersed at the velocities encountered in most boilers, enabling efficient removal during blowdown.

Typical examples of sludge dispersants are tannins, lignins, starches and certain synthetic polymers, such as the polyacrylates.

Soda Ash or Caustic Treatment

In this process, sodium carbonate, sodium hydroxide, or both are added to the boiler water to supplement the alkalinity supplied by the makeup water, which is not softened. The sodium carbonate results in the precipitation of calcium ions as calcium carbonate. The addition of caustic elevates the pH, causing the precipitation of magnesium and silica as magnesium hydroxide and magnesium silicate.

Sludge dispersants are often used in this process to prevent deposit formation.

This method of treatment is only used with boilers operating below 250 psi which utilize high hardness feedwaters.

Chelating Agents

Chelating agents are materials such as EDTA which form soluble, complex ions with calcium and magnesium. Thus, precipitation is prevented and the calcium and magnesium ions are effectively maintained in solution.

The cost of chelating agents limits their use to very low hardness feedwaters (usually 5 ppm).

Over treatment by even 1-2 ppm in the feedwater can result in a buildup of chelant concentration to very high levels in the boiler. Over a period of several months the chelant will attack metal resulting in general thinning corrosion, especially in stressed areas. Therefore, addition of chelating agents must be very carefully controlled.

Corrosion Control

Pitting corrosion in boilers is usually caused by dissolved oxygen. Caustic embrittlement can also occur which can result in catastrophic failure.

Oxygen Corrosion

Oxygen scavengers are used to remove dissolved oxygen and prevent corrosion due to its presence. Catalyzed sodium sulfite or hydrazine are commonly used. Scavengers are discussed under Water Processing Technologies.

Unreacted hydrazine can decompose at elevated temperatures yielding ammonia and nitrogen. Ammonia in the presence of small amounts of oxygen will result in the corrosion of copper alloys. For this reason, it is important not to maintain excessive hydrazine residuals.

Caustic Embrittlement

When ordinary carbon steels or austenitic stainless steels are stressed and placed in contact with hot water containing a high concentration of hydroxyl ions, intergranular cracking can occur, resulting in failure. This type of failure is referred to as caustic embrittlement and is a form of stress corrosion cracking.

In order for caustic embrittlement to occur, four conditions are necessary:

1. Hydroxides must be present in the boiler water. The use of caustic or sodium carbonate (which can decompose at elevated temperatures to yield hydroxyl ions) is a major contributor.
2. A joint or seam into which the water can leak must be present.
3. Concentration of the boiler water must occur within this seam.
4. The steel exposed to this concentrated solution must be stressed.

The presence of cracks or seams and large residual stresses can be reduced by proper design. However, it can still be a problem, especially at tube ends.

All boilers should be tested using an Embrittlement Detector such as the one designed by U. S. Bureau of Mines. If cracking tendencies are detected, treatment utilizing phosphates or sodium nitrite should be initiated.

Foaming

Foaming results in water being carried from the boiler with the steam. It is influenced by several factors, including:

1. Water level in the boiler
2. Dissolved solids concentration
3. Suspended solids in the water

Foaming can be prevented or reduced by boiler blowdown, a complete change of boiler water, or by the addition of antifoamers.

Use of antifoamers as a routine part of internal treatment is good practice. However, the use of excessive amounts can actually cause foaming and should be avoided.

BOILER BLOWDOWN

When steam is generated, essentially pure water vapor is discharged from the boiler, leaving all dissolved and suspended solids behind in the boiler. Therefore, the solids concentration in the liquid water in the boiler continuously increases as the water evaporates. In order to maintain the dissolved solids content below the allowable maximum, some of the concentrated water must be removed from the boiler and replaced with water containing a lower amount of dissolved solids. The water removed from the boiler is called blowdown.

In order to hold the dissolved solids content at an acceptable level the amount of solids removed by blowdown must equal the amount entering the boiler with the feedwater. This is illustrated in Figure 11.1.

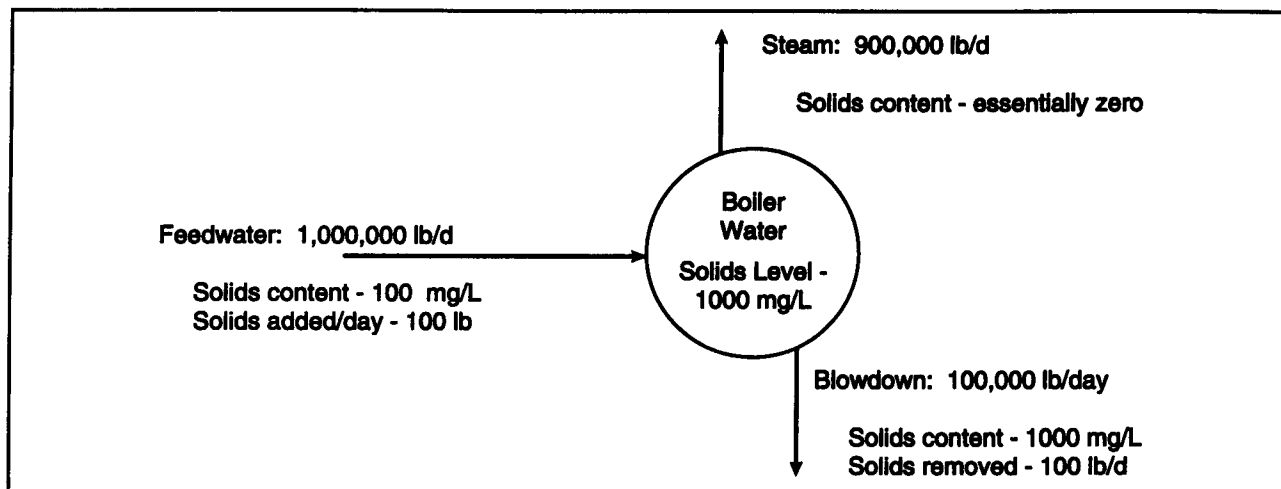


Figure 11.1 Control of Boiler Water Solids by Blowdown (Courtesy Nalco Chemical Co.)

Guidelines for maximum levels of key constituents in boiler waters recommended by the ABMA were given in Table 11.0. The desired maximum levels can be maintained by continuous blowdown.

The required amount can be calculated from the following formula:

$$B = \frac{TDS_f}{TDS_{max}} \times 100 \quad (11.1)$$

Where:

- B = Blowdown, % of feedwater
- TDS_f = Total dissolved solids in feedwater, ppm
- TDS_{max} = Maximum allowable dissolved solids in boiler water, ppm

The total dissolved solids can be estimated from conductivity measurements. Chloride concentrations are often used in place of TDS values when the feedwater composition is relatively constant. Silica content can also be used if it is the limiting factor.

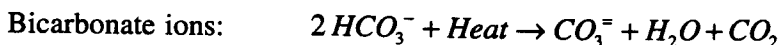
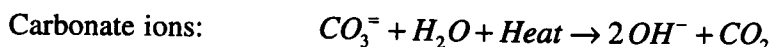
CONDENSATE RETURN SYSTEMS

Once steam leaves the boiler and is used for its intended purpose, heat will be lost and the steam will condense and form hot water. This condensed water is called condensate, and all or a portion of it is usually returned to the boiler as feedwater.

Corrosion

Although condensate is essentially distilled water, it is usually quite corrosive due to the presence of carbon dioxide. Oxygen may also be present due to leaks in the condensate lines, poor oxygen removal from the original feedwater, or exposure to the atmosphere in open condensate receiving tanks.

The primary source of carbon dioxide in steam systems is the thermal decomposition of carbonate and bicarbonate ions in the feedwater.



Only about 80% of the carbonate ions convert to hydroxyl ions and carbon dioxide. Therefore, 1 ppm of $CO_3^{=}$ will produce 0.58 ppm of CO_2 .

The bicarbonate decomposition to form carbonate ions, water and carbon dioxide is 100% complete. This means that 1 ppm of bicarbonate ion will produce 0.36 ppm of CO_2 plus 0.49 ppm carbonate ion. When the carbonate ion decomposes (assuming 80% completion), an additional 0.29 ppm CO_2 is created, giving a total of 0.65 ppm CO_2 for every ppm of bicarbonate ion which decomposes.

When alkalinities are expressed as equivalent $CaCO_3$, the following factors apply:

1. One ppm of $CO_3^{=}$ (as $CaCO_3$) will form 0.35 ppm CO_2 .
2. One ppm of HCO_3^{-} (as $CaCO_3$) will form a total of 0.79 ppm CO_2 .

This assumes that the carbonate decomposition is 80% complete.

When the steam condenses, the carbon dioxide dissolves in the condensed water, increasing its corrosivity.

Condensate return systems can be chemically treated to prevent corrosion by dissolved carbon dioxide by using neutralizing or filming amines. Ammonia can also be used, but it has the disadvantage of attacking copper or brass.

When a large portion of the steam condensate is returned to the boiler feedwater, the condensate must be deaerated (degassed) to remove the carbon dioxide and keep it from accumulating in the system.

Oil Contamination

Oil is hazardous in boilers because it forms a heat insulating film. There are normally two major sources of oil contamination in plants and facilities:

1. Reciprocating pump discharge.
2. Condensation and recovery of the still stripping steam.

Emulsified oil can be removed with DE filters and a variety of other methods. Free oil can be removed in a skimming tank.

REFERENCES

- 11.1 Ostroff, A. G.: *Introduction to Oilfield Water Technology*, Second Edition, National Association of Corrosion Engineers, Houston, Texas (1979).
- 11.2 Kemmer, Frank N., Editor: *The Nalco Water Handbook*, McGraw Hill, New York (1979).
- 11.3 Betz: *Betz Handbook of Industrial Water Conditioning*, Seventh Edition, Betz Laboratories, Inc., Trevose, Pa. (1976).

NOTES:

PRODUCTION/PROCESSING FACILITIES

Although the emphasis in this book is on the injection of water into the ground, much of the information presented applies also to surface facilities. What follows is a summary of some of the most important considerations. Further details are to be found in Volumes 1, 2 and 4 of *Gas Conditioning and Processing*, companion books in the Campbell Petroleum Series.

With surface facilities the presence of water can result in one or more of the following:

- Scale formation
- Erosion/Corrosion
- Chloride cracking (with saline water)
- Sulfide stress cracking (with sour systems)
- Plugging

Erosion and corrosion are commonly combined because in piping and vessels it is almost impossible to distinguish between the two. Control of velocity and impingement are important mechanical design details.

All of the above have been discussed previously, but there are some considerations unique to surface facilities. The amount of water being handled is significantly less than in most reservoir systems. Therefore, it is economically viable to treat it more thoroughly.

HEAT EXCHANGERS AND HEATERS

Water cooled heat exchangers are used commonly for the cooling of gas, dehydration and sweetening liquids, and hot hydrocarbon liquids prior to storage. The discussion on cooling water treatment in Chapter 10 applies to heat exchangers using such water. Water from lakes, rivers and the oceans also are used extensively for cooling.

An exchanger cannot be properly specified and designed until the cooling water properties have been determined reliably. What kind of exchanger is feasible with the kind of water available? It often is not practical (mechanically or economically) to eliminate all five problems listed above.

The combination of process requirements and water quality may dictate that scale formation cannot be eliminated, only its rate of formation can be controlled. Reduction of pH to prevent calcium carbonate scale may introduce metallurgical problems. Many questions are pertinent. What kind of scales are anticipated? Can these scales be removed by available chemical cleaners or is mechanical

scraping required? How often will cleaning be required? The final choice of heat exchanger type should represent an intelligent answer to questions like these as well as those raised by process concerns.

If a tube-and-shell exchanger is considered, should the water be placed on the tube side or the shell side? The tube side is easier to clean. Final process calculations cannot proceed until such decisions are made. A plate type exchanger might be preferred because it can be disassembled for mechanical cleaning.

Erosion/corrosion can dictate the use of metals that are poor conductors of heat or are difficult to fabricate. Stainless steels, for example, are poor conductors of heat. Their use reduces thermal efficiency. Titanium is a good heat conductor but is expensive to fabricate. Fortunately, there are applications where titanium may be used economically in plate exchangers.

As referred to earlier in this book, chloride cracking can be a problem when the chloride ion is present in the water. Above about 150°F [65°C], a commonly used material like Type 316 stainless steel is not satisfactory for cooling with sea water. Titanium in a plate exchanger is a more satisfactory choice near, or above, this temperature. Of course, in a typical sea water, temperature in excess of 150°F [65°C] are usually well above the calcium carbonate scaling temperature. Usually it is not economical to treat sea water to prevent scale formation in offshore process applications if the air is cold enough for aerial cooling. With compressors or other "hot" equipment, *aerial cooling* is most always the choice offshore in temperate climates. This pretty well eliminates concern about chloride cracking and scaling in heat exchange with such equipment.

In tropical climates where the air is warm and/or applications where low temperatures are desired (like dehydration), water cooling may be the preferred choice.

A "once-through" system using raw sea water is very satisfactory if temperature and metallurgical constraints are adhered to. At least minimal filtration is necessary to prevent the ingress of marine organisms, even though initial tests may indicate their absence. The marine structure acts as an artificial reef for their development and they could become a problem. However, process tubing and piping is not as prone to plug as a reservoir rock. In some cases a coarse screen to keep out large creatures, with no chlorination, may be satisfactory. If a filter is used, chlorination is necessary to control bacterial growth and fouling in the filtration system.

Deoxygenation of sea water is not always carried out when the only use is process cooling, since corrosion can be economically controlled by utilizing corrosion resistant materials.

The use of saline underground water for cooling involves the same considerations if it is not "sour" with sulfur compounds. If the latter are present, the later discussion for sour systems applies.

Once-through cooling from fresh water sources is largely a scale prevention problem.

Indirect Heaters

This is any device where heat from the burner and combustion gas transfers to a liquid bath which, in turn, transfers heat to another medium. A water bath heater is used commonly to heat gas or oil. In a typical installation the temperature of the surface of the burner tube in contact with the water is over 200°F [93°C], well above the scaling temperature of many salts present in water.

Check the water used to fill the heater. Raw water seldom is good enough. This is a batch process so proper treatment is inexpensive. However, like your automobile radiator, it is a good idea to change the treated water periodically. With most heaters of this kind it is convenient to check periodically for scale formation on the fire tube.

SOUR SYSTEMS

Sour systems require considerations discussed earlier in this book. Hydrogen sulfide (H_2S) is not corrosive in the absence of liquid water until the system temperature reaches about 550°F [288°C]. Thus, if liquid water can be eliminated or inhibited, only heaters represent a common problem.

The use of *dehydration* to eliminate liquid water is common. Aqueous solutions of chemicals like the *amines* can effectively remove the sulfur compounds. Figure 12.1 summarizes some of the problems encountered in these types of units as well as others commonly used with sour systems. Discussions about corrosion testing, corrosion inhibitors, etc., in early chapters apply equally well for these systems.

There are several concerns that apply for all sour process systems.

Mechanical

Normal liquid velocity in process lines will be 8-10 ft/sec. Reducing this velocity to 3.0-3.5 ft/sec in a sour system will minimize erosion/corrosion and facilitate the effectiveness of a filming-type corrosion inhibitor. Long radius ells are preferred to minimize *impingement effects*. Stress relieved, butt-welded pipe joints are preferred to threaded joints. Avoid the use of dissimilar metals to minimize *bimetallic corrosion*.

Control valves should have "soft seats" to compensate for *embrittlement*. A Rockwell hardness of 18-20 usually is preferred.

Metallurgy

With proper attention to mechanical details like those above and proper *stress relief* of *all* welded parts, carbon steel plants have proven satisfactory where initial cost was an important factor. Many plants use Type 304 and 316 stainless steel at critical points. Metal-clad and plastic coated parts also are being used. Type 7072 aluminum-clad tubing has been employed. But, regardless of the metallurgy chosen, it is recommended that you limit velocities, impingement, etc.

Inhibition

The use of a proper inhibitor is almost always desirable in sour production/processing systems. Normally it will be of the filming type. The usual goal is to reduce corrosion, not to eliminate it.

Figure 12.2 shows the combined effect of cooling and adding a corrosion inhibitor to one triethylene glycol (TEG) dehydration unit.

SUMMARY

This chapter and the ones which immediately precede it give a brief overview of various applications which require a reasonable knowledge about how water behaves in petroleum systems and how to handle it effectively. Water occurs in all petroleum reservoirs. Ignoring it, or handling it improperly, oftentimes is a hidden cost. Nevertheless, it is a tremendous one. Greater efficiency, lower overhead and greater profit are the end result of improved water handling. This book is dedicated to that proposition.

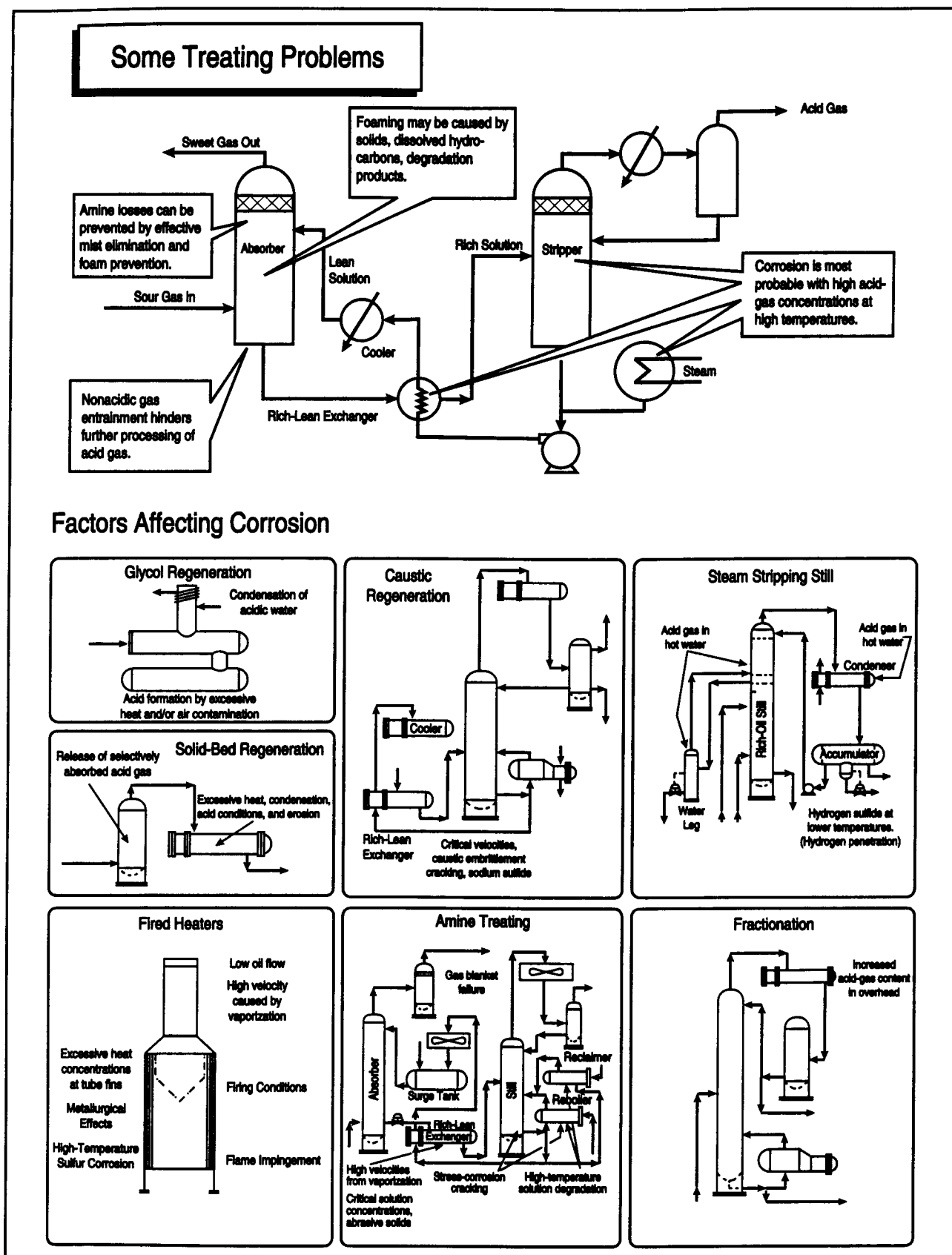


Figure 12.1 Summary of Problem Points in Sour Gas Treating

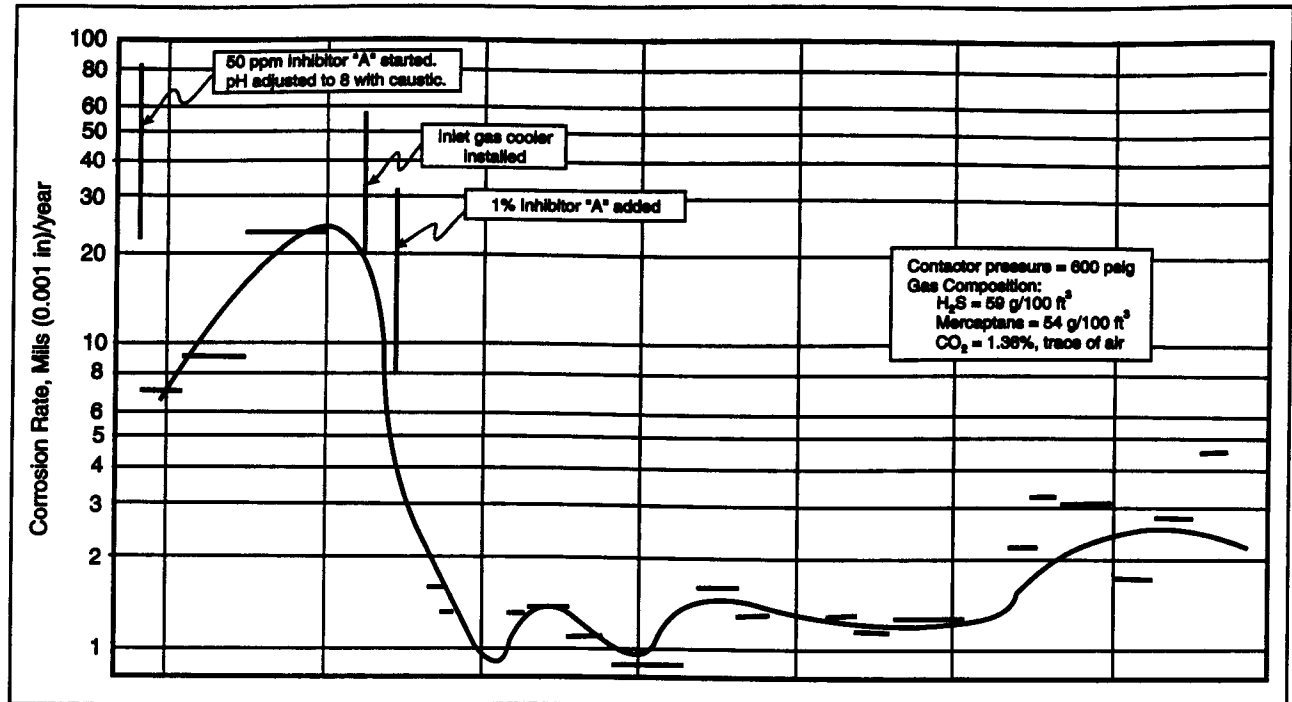


Figure 12.2 Possible Effect of Corrosion Inhibitors in TEG Systems

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APPENDIXES

APPENDIX 1

Selected Elements, Symbols and Atomic Weights

Element	Symbol	Atomic Weight*
Aluminum	Al	27.0
Barium	Ba	137.3
Calcium	Ca	40.1
Carbon	C	12.0
Chlorine	Cl	35.5
Chromium	Cr	52.0
Cobalt	Co	58.9
Copper	Cu	63.5
Flourine	F	19.0
Gold	Au	197.0
Hydrogen	H	1.0
Iron	Fe	55.8
Magnesium	Mg	24.3
Manganese	Mn	54.9
Mercury	Hg	200.6
Nickel	Ni	58.7
Nitrogen	N	14.0
Oxygen	O	16.0
Phosphorus	P	30.0
Potassium	K	39.1
Sodium	Na	23.0
Strontium	Sr	87.6
Sulfur	S	32.1
Zinc	Zn	65.4
* Rounded off to one decimal		

APPENDIX 2

Selected Ions, Compounds and Equivalent Weights

Cations	Symbol	Equivalent Weight	Anions	Symbol	Equivalent Weight
Barium	Ba ⁺⁺	68.7	Bicarbonate	HCO ₃ ⁻	61.0
Calcium	Ca ⁺⁺	20.0	Carbonate	CO ₃ ⁼	30.0
Hydrogen	H ⁺	1.0	Chloride	Cl ⁻	35.5
Iron			Hydroxyl	OH ⁻	17.0
– Ferrous	Fe ⁺⁺	27.9	Oxide	O ⁼	8.0
– Ferric	Fe ⁺⁺⁺	18.6	Phosphate	PO ₄ ⁼	31.6
Magnesium	Mg ⁺⁺	12.2	Sulfate	SO ₄ ⁼	48.0
Sodium	Na ⁺	23.0	Sulfide	S ⁼	16.0
Strontium	Sr ⁺⁺	43.8	Sulfite	SO ₃ ⁼	40.0

Compounds & Gases	Symbol	Valence	Equivalent Weight
Barium Sulfate	BaSO ₄	2	117.0
Calcium Carbonate	CaCO ₃	2	50.0
Calcium Sulfate	CaSO ₄	2	68.0
Chlorine	Cl ₂	2	35.5
Ferrous Carbonate	FeCO ₃	2	58.0
Ferric Oxide	Fe ₂ O ₃	6	26.6
Oxygen	O ₂	4	8.0
Carbon Dioxide	CO ₂	4	11.0
Sodium Bicarbonate	NaHCO ₃	1	84.0
Sodium Chloride	NaCl	1	58.5

APPENDIX 3
Selected Conversion Factors

SI	English	English	SI
1 μm	0.039 mil	1 mil	25.4 μm
1 m	39.37 in	1 in	0.0254 m
1 m	3.28 ft	1 ft	0.3048 m
1 km	3280 ft	1 ft	0.0003 km
1 km	0.62 mile	1 mile	1.61 km
1 mm/y	39.37 mpy	1 mpy	0.0254 mm/y
1 $\mu\text{m}/\text{y}$	0.039 mpy	1 mpy	25.4 $\mu\text{m}/\text{y}$
1 m/s	3.28 ft/s	1 ft/s	0.305 m/s
1 m^2	10.76 ft^2	1 ft^2	0.093 m^2
1 m^3	35.3 ft^3	1 ft^3	0.0283 m^3
1 m^3	6.29 API bbl	1 API bbl	0.159 m^3
1 L	0.0353 ft^3	1 ft^3	28.3 L
1 L	0.264 US gal	1 US gal	3.785 L
1 L	0.629 API bbl	1 API bbl	1.59 L
1 m^3/m^3	5.61 $\text{ft}^3/\text{API bbl}$	1 $\text{ft}^3/\text{API bbl}$	0.178 m^3/m^3
1 $\text{m}^3/\text{hr}/\text{m}^2$	0.41 USgpm/ ft^2	1 USgpm/ ft^2	2.44 $\text{m}^3/\text{hr}/\text{m}^2$
1 bar = 100 kPa	14.5 psi	1 psi	6.897 kPa

English Unit Conversions	
1 API bbl	42 gal US
1 API bbl	35 gal Imperial
1 API bbl	5.6 ft^3
1000 bbl/day	29.2 USgpm
1 US gal	0.134 ft^3
1 USgpm	34.3 bbl/day
1 mil	0.001 in

Temperature Conversion Chart

NOTE: The numbers in boldface refer to the temperature in degrees, either Centigrade or Fahrenheit, which it is desired to convert into the other scale. If converting from Fahrenheit to Centigrade degrees, the equivalent temperature will be found in the left column; while if converting from degrees Centigrade to degrees Fahrenheit, the answer will be found in the column on the right.

°C			°F			°C			°F			°C			°F		
-73.3	-100	-148.0	2.8	37	98.6	33.3	92	197.6		293	560	1040					
-67.8	-90	130.0	3.3	38	100.4	33.9	93	199.4		299	570	1058					
-62.2	-80	-112.0	3.9	39	102.2	34.4	94	201.2		304	580	1076					
-59.4	-75	-103.0	4.4	40	104.0	35.0	95	203.0		310	590	1094					
-56.7	-70	-94.0	5.0	41	105.8	35.6	96	204.8		316	600	1112					
-53.9	-65	-85.0	5.6	42	107.6	36.1	97	206.6		321	610	1130					
-51.1	-60	-76.0	6.1	43	109.4	36.7	98	208.4		327	620	1148					
-48.3	-55	-67.0	6.7	44	111.2	37.2	99	210.2		332	630	1166					
-45.6	-50	-58.0	7.2	45	113.0	37.8	100	212.0		33	640	1184					
-42.8	-45	-49.0	7.8	46	114.8	43	110	230		343	650	1202					
-40.0	-40	-40.0	8.3	47	116.6	49	120	248		349	660	1220					
-37.2	-35	-31.0	8.9	48	118.4	54	130	266		354	670	1238					
-34.4	-30	-22.0	9.4	49	120.2	60	140	284		360	680	1256					
-31.7	-25	-13.0	10.0	50	122.0	66	150	302		366	690	1274					
-28.9	-20	-4.0	10.6	51	123.8	71	160	320		371	700	1292					
-26.1	-15	5.0	11.1	52	125.6	77	170	338		377	710	1310					
-23.3	-10	14.0	11.7	53	127.4	82	180	356		382	720	1328					
-20.6	-5	23.0	12.2	54	129.2	88	190	374		388	730	1346					
-17.8	0	32.0	12.8	55	131.0	93	200	392		393	740	1364					
-17.2	1	33.8	13.3	56	132.8	99	210	410		399	750	1382					
-16.7	2	35.6	13.9	57	134.6	100	212	414		404	760	1400					
-16.1	3	37.4	14.4	58	136.4	104	220	428		410	770	1418					
-15.6	4	39.2	15.0	59	138.2	110	230	446		416	780	1436					
-15.0	5	41.0	15.6	60	140.0	116	240	464		421	790	1454					
-14.4	6	42.8	16.1	61	141.8	121	250	482		427	800	1472					
-13.9	7	44.6	16.7	62	143.6	127	260	500		432	810	1490					
-13.3	8	46.4	17.2	63	145.4	132	270	518		438	820	1508					
-12.8	9	48.2	17.8	64	147.2	138	280	536		443	830	1526					
-12.2	10	50.0	18.3	65	149.0	143	290	554		449	840	1544					
-11.7	11	51.8	18.9	66	150.8	149	300	572		454	850	1562					
-11.1	12	53.6	19.4	67	152.6	154	310	590		460	860	1580					
-10.6	13	55.4	20.0	68	154.4	160	320	608		466	870	1598					
-10.0	14	57.2	20.6	69	156.2	166	330	626		471	880	1616					
-9.4	15	59.0	21.1	70	158.0	171	340	644		477	890	1634					
-8.9	16	60.8	21.7	71	159.8	177	350	662		482	900	1652					
-8.3	17	62.6	22.2	72	161.6	182	360	680		488	910	1670					
-7.8	18	64.4	22.8	73	163.4	188	370	698		493	920	1688					
-7.2	19	66.2	23.3	74	165.2	193	380	716		499	930	1706					
-6.7	20	68.0	23.9	75	167.0	199	390	734		504	940	1724					
-6.1	21	69.8	24.4	76	168.8	204	400	752		510	950	1742					
-5.6	22	71.6	25.0	77	170.6	210	410	770		516	960	1760					
-5.0	23	73.4	25.6	78	172.4	216	420	788		521	970	1778					
-4.4	24	75.2	26.1	79	174.2	221	430	806		527	980	1796					
-3.9	25	77.0	26.7	80	176.0	227	440	824		532	990	1814					
-3.3	26	78.8	27.2	81	177.8	232	450	842		538	1000	1832					
-2.8	27	80.6	27.8	82	179.6	238	460	860		566	1050	1922					
-2.2	28	82.4	28.3	83	181.4	243	470	878		593	1100	2012					
-1.7	29	84.2	28.9	84	183.2	249	480	896		621	1150	2102					
-1.1	30	86.0	29.4	85	185.0	254	490	914		649	1200	2192					
-0.6	31	87.8	30.0	86	186.8	260	500	932		677	1250	2282					
0.0	32	89.6	30.6	87	188.6	266	510	950		704	1300	2372					
0.6	33	91.4	31.1	88	190.4	271	520	968		732	1350	2462					
1.1	34	93.2	31.7	89	192.2	277	530	986		760	1400	2552					
1.7	35	95.0	32.2	90	194.0	282	540	1004		788	1450	2642					
2.2	36	96.8	32.8	91	195.8	288	550	1022		816	1500	2732					

The formulas below may also be used for converting Centigrade or Fahrenheit degrees into the other scale

$$\text{Degrees Centigrade, } ^\circ\text{C} = \frac{5}{9} (^{\circ}\text{F} + 40) - 40$$

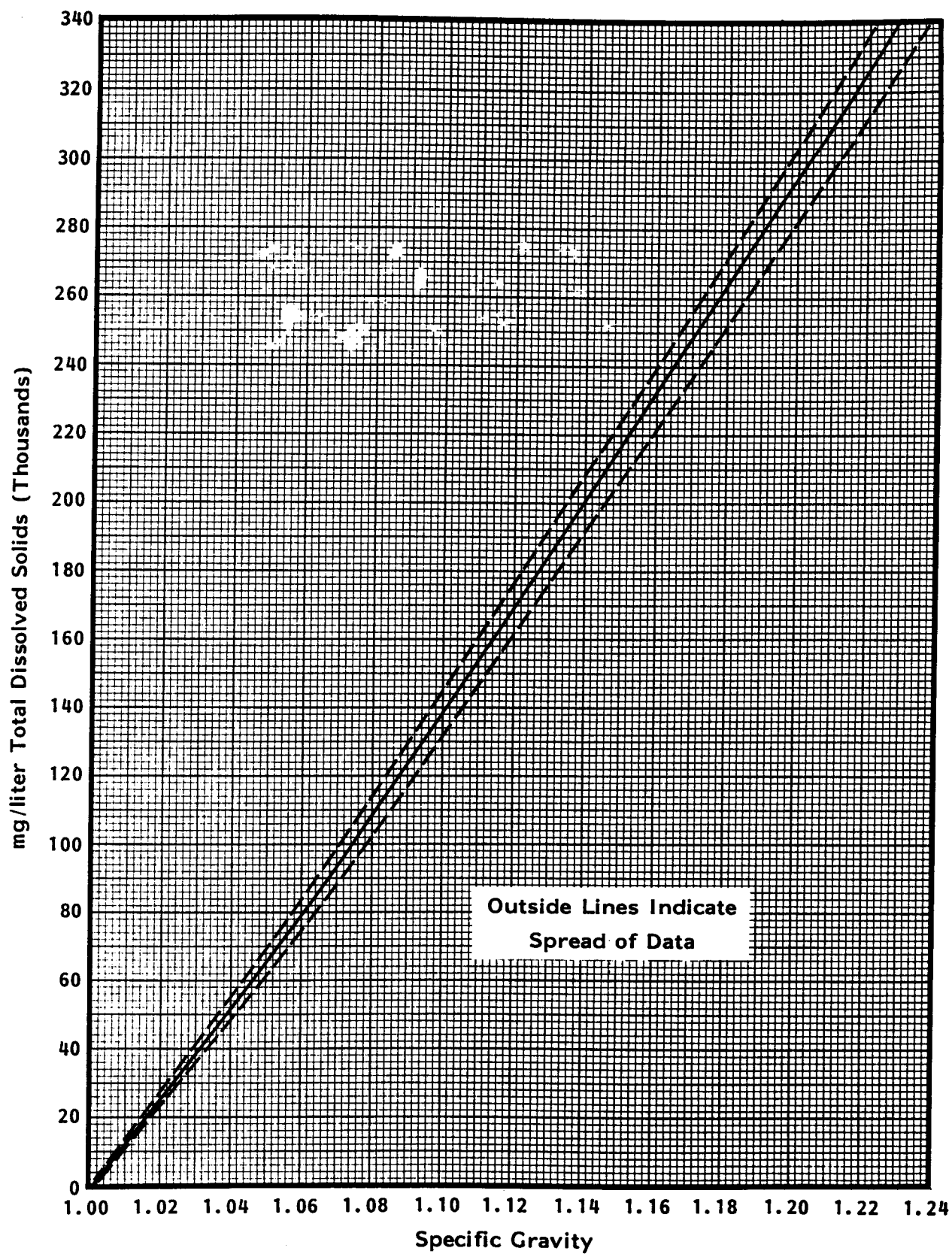
$$\text{Degrees Fahrenheit, } ^\circ\text{F} = \frac{9}{5} (^{\circ}\text{C} + 40) - 40$$

APPENDIX 5
Water Sample Description

Field:	Lease:
County:	Well:
State:	
Date Sample Taken:	
Person Taking Sample:	
Sample Point Location:	
Sample Description	
Source:	(Geologic Formation, River, etc.)
Color:	
Odor:	
Suspended Solids:	
Oil Scum:	
System Operation at Time of Sampling (Check One)	
Normal:	
Abnormal (Describe):	
Shut-Down:	
Analyses Performed On-Site(List):	

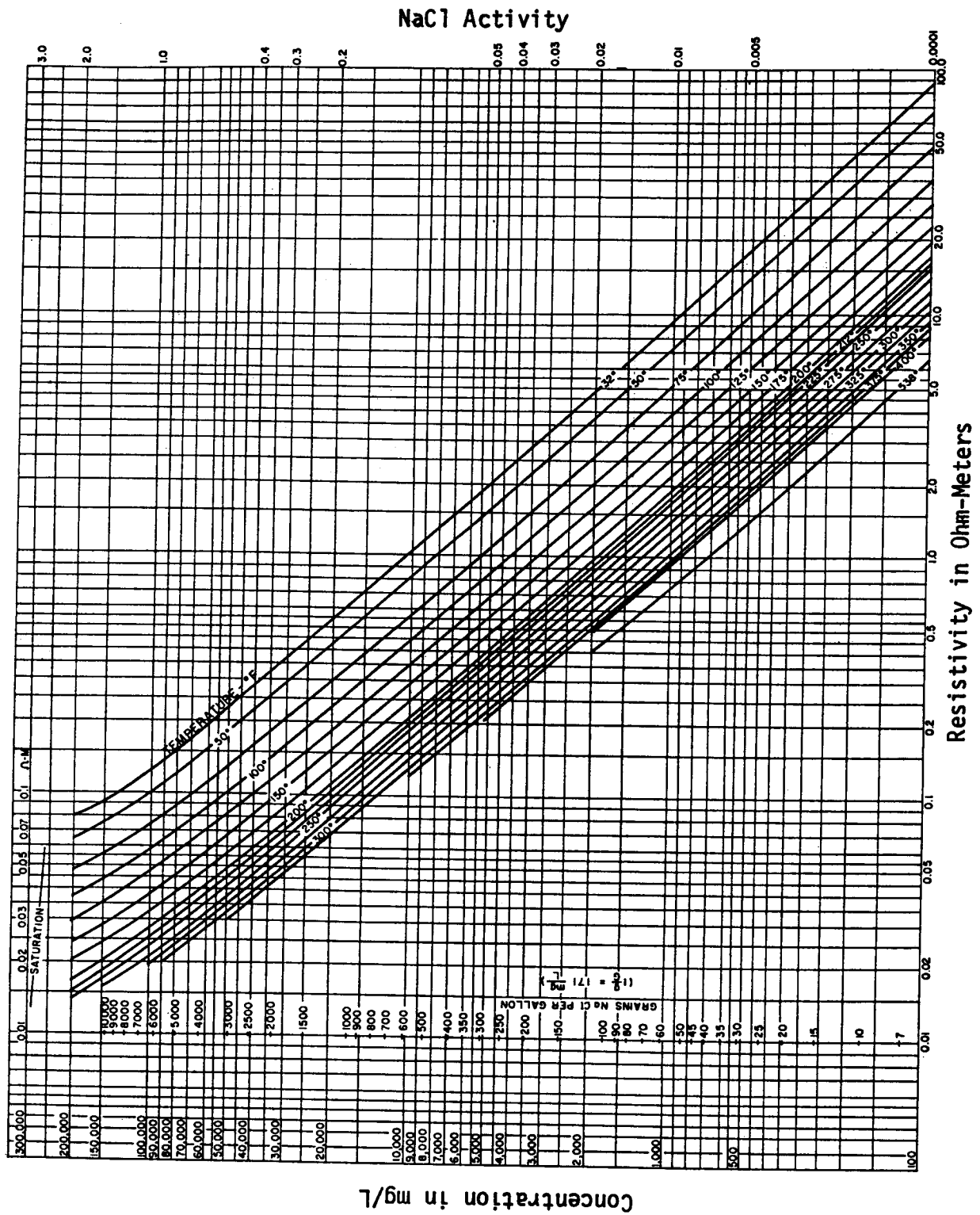
APPENDIX 6

Specific Gravity vs. Total Dissolved Solids



APPENDIX 7

Resistivity as a Function of Salinity and Temperature for NaCl Solutions



APPENDIX 8

Calcium Carbonate Conversion Factors

To Convert From	To	Ion	Multiply By
ppm as CaCO ₃	ppm of the Ion	Ca ⁺⁺	0.400
		Mg ⁺⁺	0.243
		K ⁺	0.782
		Na ⁺	0.460
		Ba ⁺⁺	1.374
		Sr ⁺⁺	0.876
		Fe ⁺⁺	0.558
		Fe ⁺⁺⁺	0.372
		Cl ⁻	0.709
		HCO ₃ ⁻	1.220
		OH ⁻	0.340
		SO ₄ ⁼	0.960
		CO ₃ ⁼	0.600
Conversion Factor = $\frac{\text{Equivalent Wt. of Ion}}{\text{Equivalent Wt. of CaCO}_3} = \frac{\text{Equivalent wt. of Ion}}{50}$			

APPENDIXES

APPENDIX 9

Water Analysis Reports

PRODUCTION PROFITS, INC.

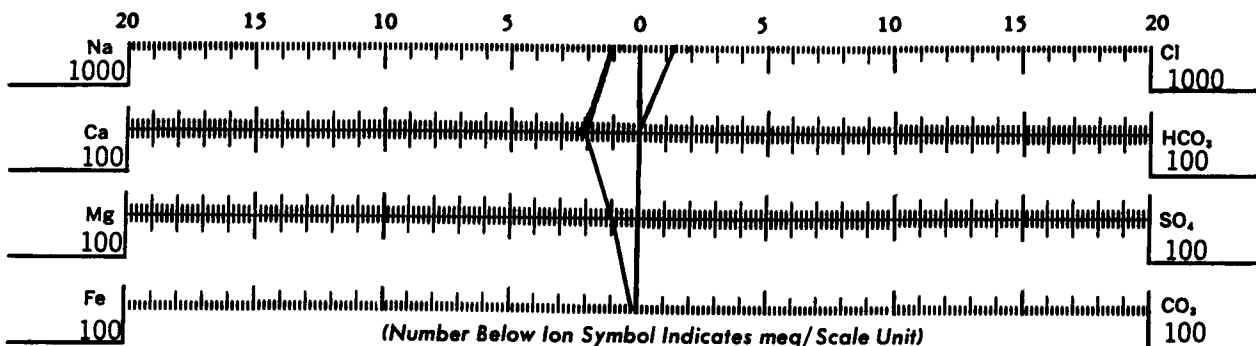
Petroleum Service Laboratory
DALLAS, TEXAS

Client _____
County _____ State _____
Field _____ Lease _____ Well No. _____
Formation _____ Depth _____ Perf. _____
Source of Sample Injection Pump Discharge (Produced)
Date Collected 12/4/86 by PPI

REPORT OF WATER ANALYSIS

Lab. Number G1 4014 Specific Gravity 1.0632 pH (Lab) 6.5
Total Dissolved Solids 84,155 Resistivity (Ohmmeters at 68° F.) 0.098 Hydrogen Sulfide Absent

DISSOLVED MINERAL ANALYSIS PATTERN



DISSOLVED SOLIDS ANALYSIS

	mg/L	meq/L
Total Solids (Calc.)	<u>84,155</u>	
Sodium (Calc.)	<u>26,400</u>	<u>1145.8</u>
Iron (Dissolved)	<u>16</u>	<u>0.6</u>
Barium	<u>6</u>	<u>0.1</u>
Calcium	<u>4350</u>	<u>217.1</u>
Magnesium	<u>1250</u>	<u>102.8</u>
Chloride	<u>51,700</u>	<u>1457.9</u>
Bicarbonate	<u>115</u>	<u>1.9</u>
Carbonate	<u>0</u>	<u>0</u>
Sulfate	<u>318</u>	<u>6.6</u>

TOTAL IRON 25

SOLUBILITY CALCULATIONS

Calcium Carbonate Stability Index at 77° F _____
Calcium Sulfate Stability at 95°F _____
Concentration 6.6 meq/L
Barium Sulfate Stability at 95° F _____
Concentration 0.1 meq/L

PRECIPITATED AND SUSPENDED SOLIDS ANALYSIS

	mg/L
Total Undissolved Solids	_____
Oil (Solvent Soluble)	_____
Acid Solubles	_____
Iron	as _____
Calcium	as _____
Magnesium	as _____
Sulfate	as _____
Organic (Ignition Loss)	_____
Acid Insolubles	_____
Sand & Clay	_____
Barium Sulfate	(Quan.) _____ (Qual.) _____

REMARKS

Sodium by AA: 29,390

Oil and Grease: 0 mg/L

APPENDIX 9
Water Analysis Reports (Cont'd.)

Requested By:		Sample No. GL 4014		Date Sampled 12/4/86
Field	Legal Description		Province	
Lease or Unit	Well	Depth	Formation	Rate B/D 1000
Type of Water (Produced, Supply, etc.) Produced		Sampling Point (Treater, Tank, etc.) Injection Pump Discharge		Sampled By: PPI
Sample Appearance		Clear <input checked="" type="checkbox"/>	Cloudy <input type="checkbox"/>	Colored <input type="checkbox"/>
Suspended Solids <input type="checkbox"/>		Oil Present <input type="checkbox"/>	Odor <input type="checkbox"/>	
Remarks (Any other relevant information)				

DISSOLVED SOLIDS

<u>CATIONS</u>	mg/L	me/L
Sodium, Na(calc)	26,347	1145.5
Calcium, Ca	4350	217.1
Magnesium, Mg	1250	102.8
Barium, Ba	6	0.1
Iron, Fe (Total)	25	0.9

OTHER PROPERTIES

pH	6.5
Specific Gravity, 60/60F	1.0632
Resistivity(ohm-meters) F	0.098
Sulfide as H ₂ S mg/L	Absent

ANIONS

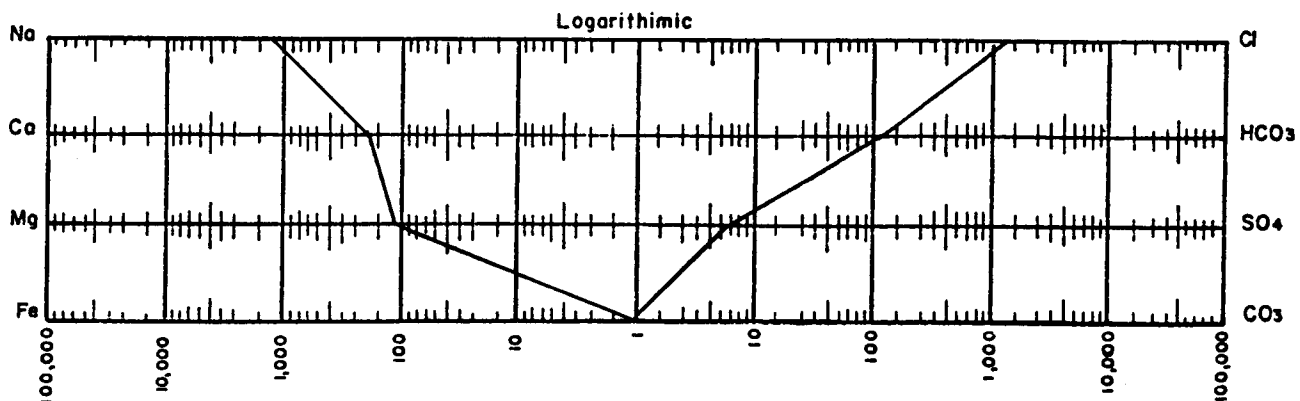
Chloride, Cl	51,700	1457.9
Sulfate, SO ₄	318	6.6
Carbonate, CO ₃	0	0
Bicarbonate HCO ₃	115	1.9

REMARKS & RECOMMENDATIONS

Total Dissolved Solids (calc.) 84,155

Analysis By: _____

WATER PATTERNS — me/L



APPENDIX 10
Use of Syringes

1. Remove the needle from the end of the syringe, immerse the tip of the syringe into the solution, and draw in a bit more solution than you plan to use.
2. Withdraw the syringe from the solution and orient it with the tip pointing up.
3. Tap the side of the syringe with your finger until all gas bubbles rise to the tip of the syringe.
4. Move the syringe plunger just far enough to displace the gas from the syringe, plus a few drops of liquid.
5. Replace the needle if necessary, and move the plunger sufficiently to force a drop or two of liquid out of the tip of the needle.
6. Move the plunger index to the desired volume and then dispense the sample or begin titration, whichever is desired.
7. Always use at least half of the syringe volume, whether measuring a sample or titrating. If less volume is required, use a smaller syringe. This is necessary to maintain the needed accuracy.

APPENDIX 11

Nomograph for Determination of Ryznar and Langelier Scaling Indexes

Example:

Given the following data, find the values of both the Langelier and the Ryznar Indexes:

pH = 6.9

Temp. = 70°F

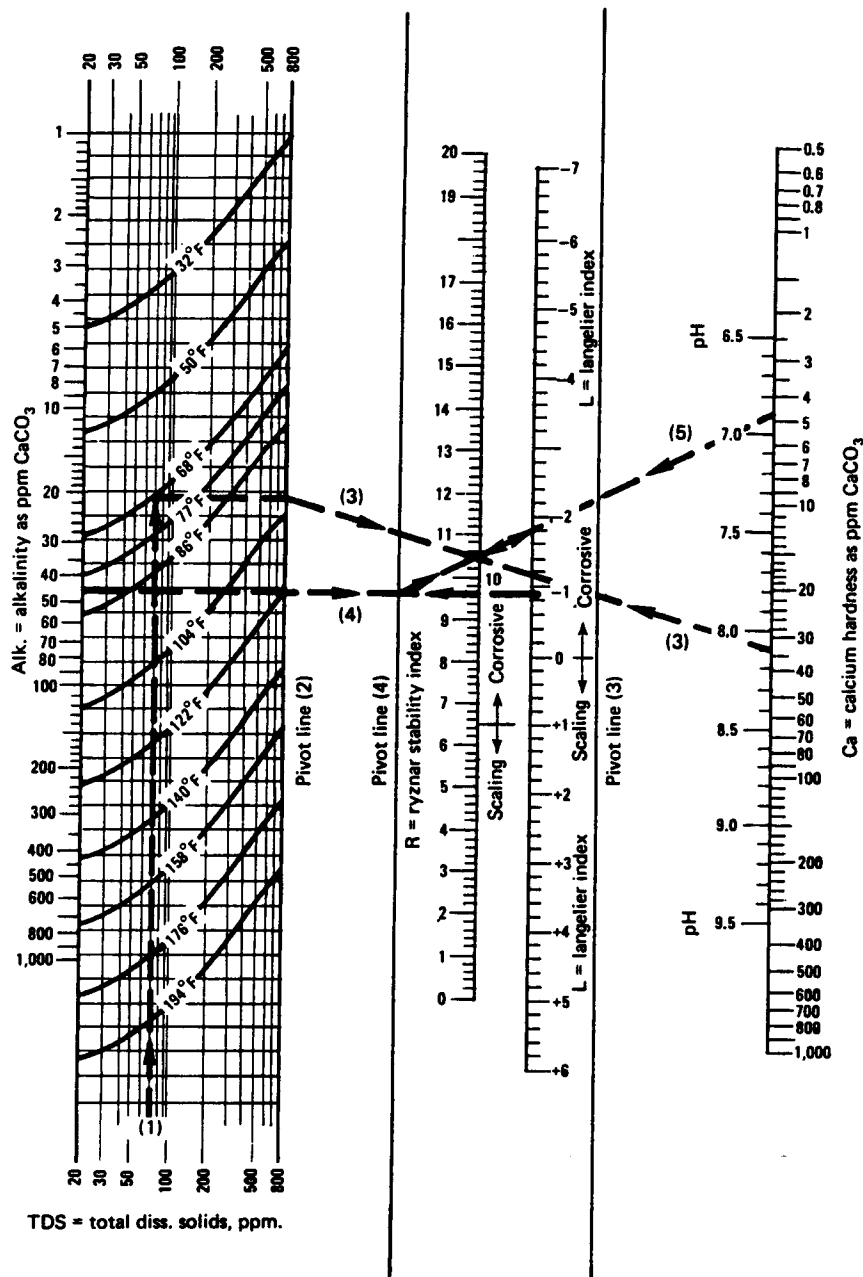
TDS = 72 ppm

Calcium hardness as CaCO_3 = 34 ppm

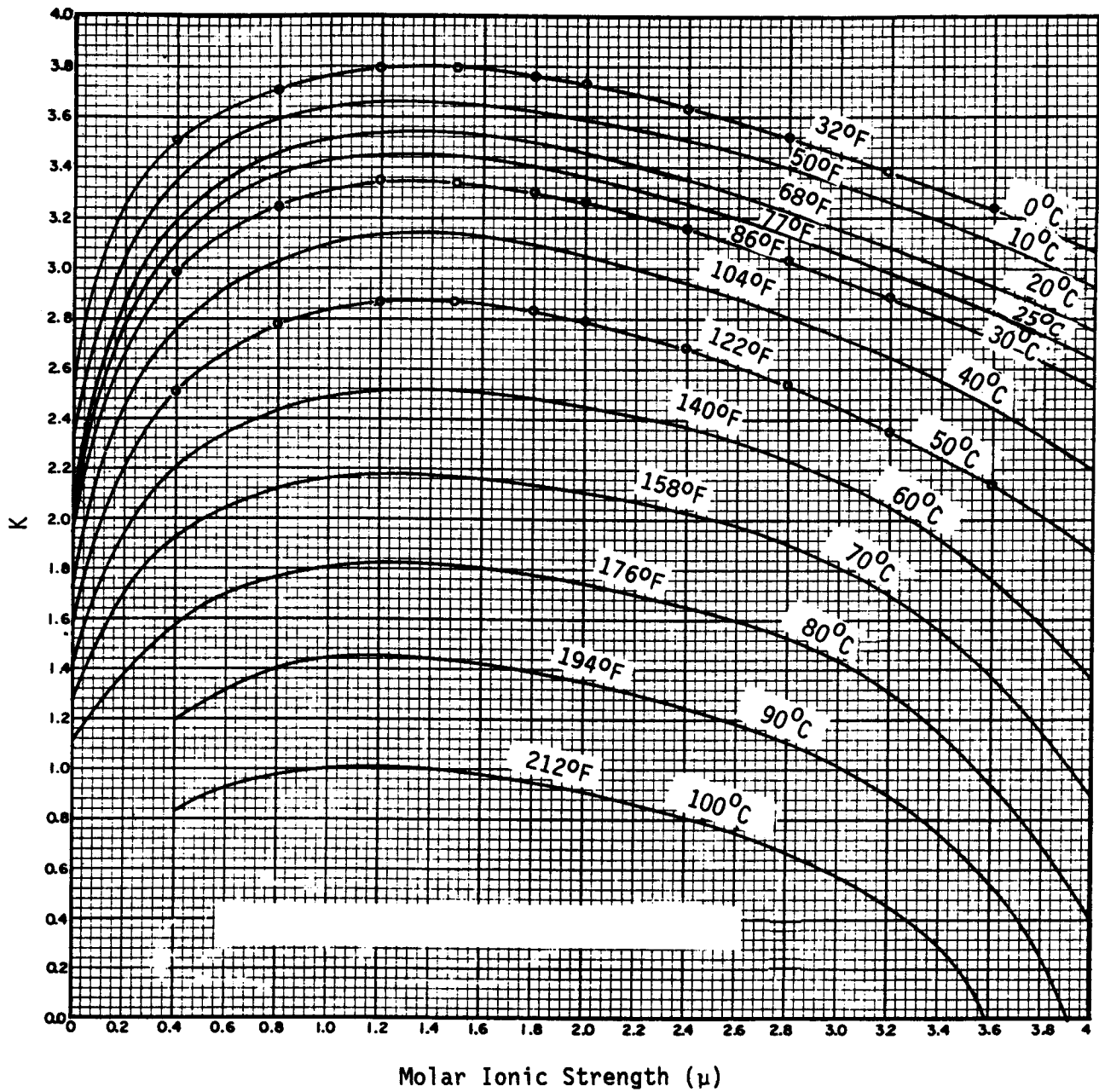
Methyl orange alkalinity as CaCO_3 = 47 ppm

Solution:

1. Reading at the bottom of the left-hand side, find TDS = 72 and note the intersection of this reading with the curved 70°F line.
2. Carry this intersection horizontally to pivot line 2.
3. Connect that point with Ca hardness = 34 on the right-hand scale.
4. Note the intersection with pivot line 3.
5. Connect that point with alkalinity = 47 on the left-hand scale.
6. Note the intersection on pivot line 4. Connect this intersection to pH = 6.9.
7. The Langelier Index = -1.8 and the Ryznar Index = 10.5. This water would be said to be very corrosive.

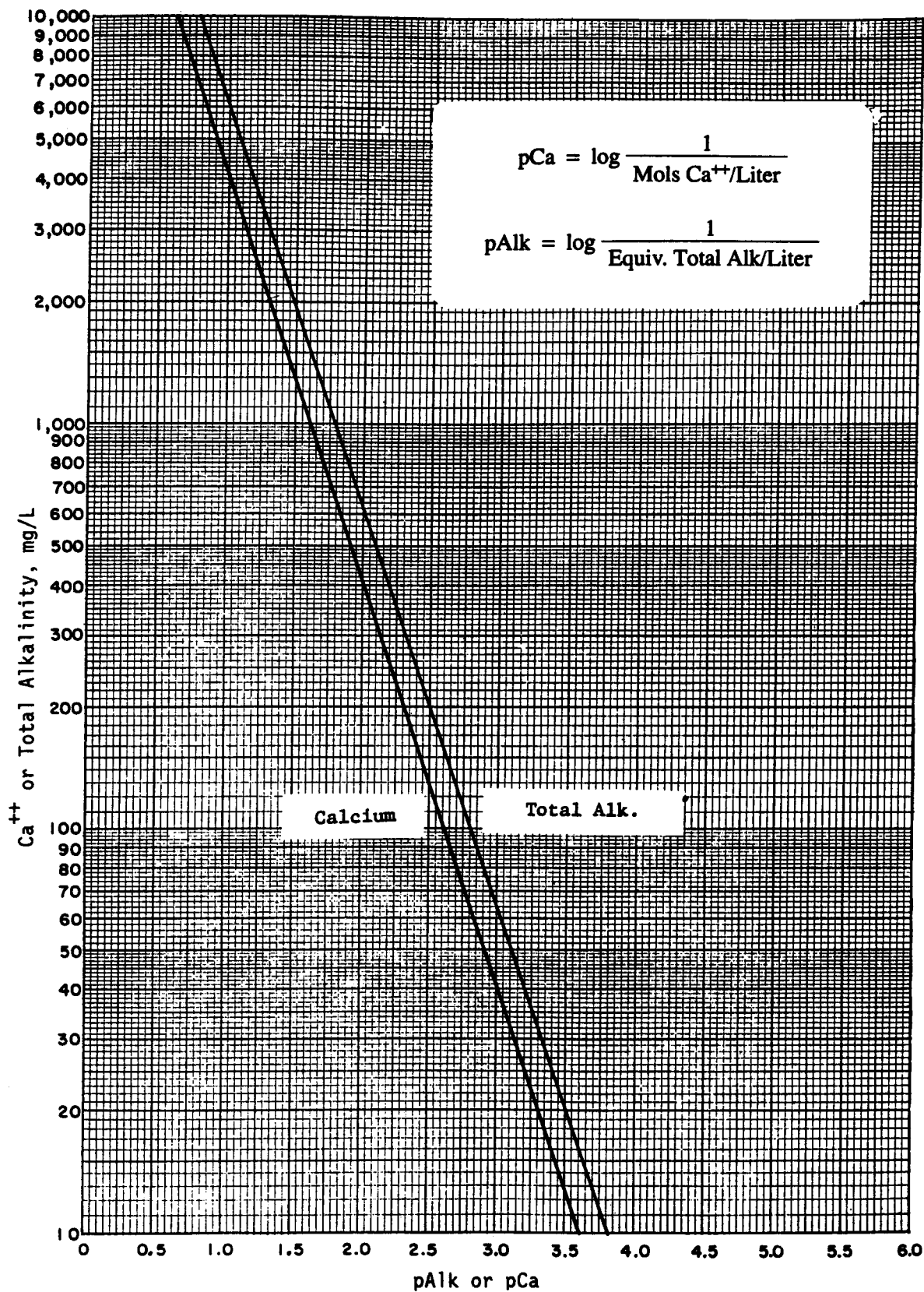


APPENDIX 12

Values of Stiff & Davis "K" for CaCO_3 Scale Calculations

APPENDIX 13

Conversion of mg/L Calcium and Alkalinity into pCa and pAlk



APPENDIX 14

Example Scale Calculations

Ionic Strength, CaCO_3 Scaling Index and CaSO_4 Solubility

Water Analysis		Ionic Strength Calculation	
Ion	Concentration (mg/L)	Conversion Factor	
Na^+	7559	2.2×10^{-5}	$= 16\,630 \times 10^{-5}$
Ca^{++}	877	5.0×10^{-5}	$= 4385 \times 10^{-5}$
Mg^{++}	239	8.2×10^{-5}	$= 1960 \times 10^{-5}$
Cl^-	12\,294	1.4×10^{-5}	$= 17\,212 \times 10^{-5}$
$\text{CO}_3^{=}$	0	3.3×10^{-5}	$= 0 \times 10^{-5}$
HCO_3^-	556	0.82×10^{-5}	$= 456 \times 10^{-5}$
SO_4^-	1740	2.1×10^{-5}	$= 3654 \times 10^{-5}$
		Total Ionic Strength = μ	$= 44\,297 \times 10^{-5}$
		μ	$= 0.44$

Temperature = 60°C ; pH = 7.04

Calcium Carbonate Scaling Index Calculation

K = 2.24 (from Appendix 12)

pCa = 1.67 (from Appendix 13)

pAlk = 2.05 (from Appendix 13)

$$\text{SI} = \text{pH} - (\text{K} + \text{pCa} + \text{pAlk}) = 7.04 - (2.24 + 1.67 + 2.05) = +1.08$$

SI > 0 , so CaCO_3 scale is likely.

Calcium Sulfate Solubility Calculation

 $K_c = 9.2 \times 10^{-4}$ (from Appendix 15) $4 K_c = 36.8 \times 10^{-4}$

Ion	Concentration (mg/L)	Conversion Factor	M (moles/L)
Ca^{++}	877	2.5×10^{-5}	2192.5×10^{-5}
$\text{SO}_4^{=}$	1740	1.04×10^{-5}	$1809. \times 10^{-5}$
$X = \Delta M = 382.9 \times 10^{-5}$			

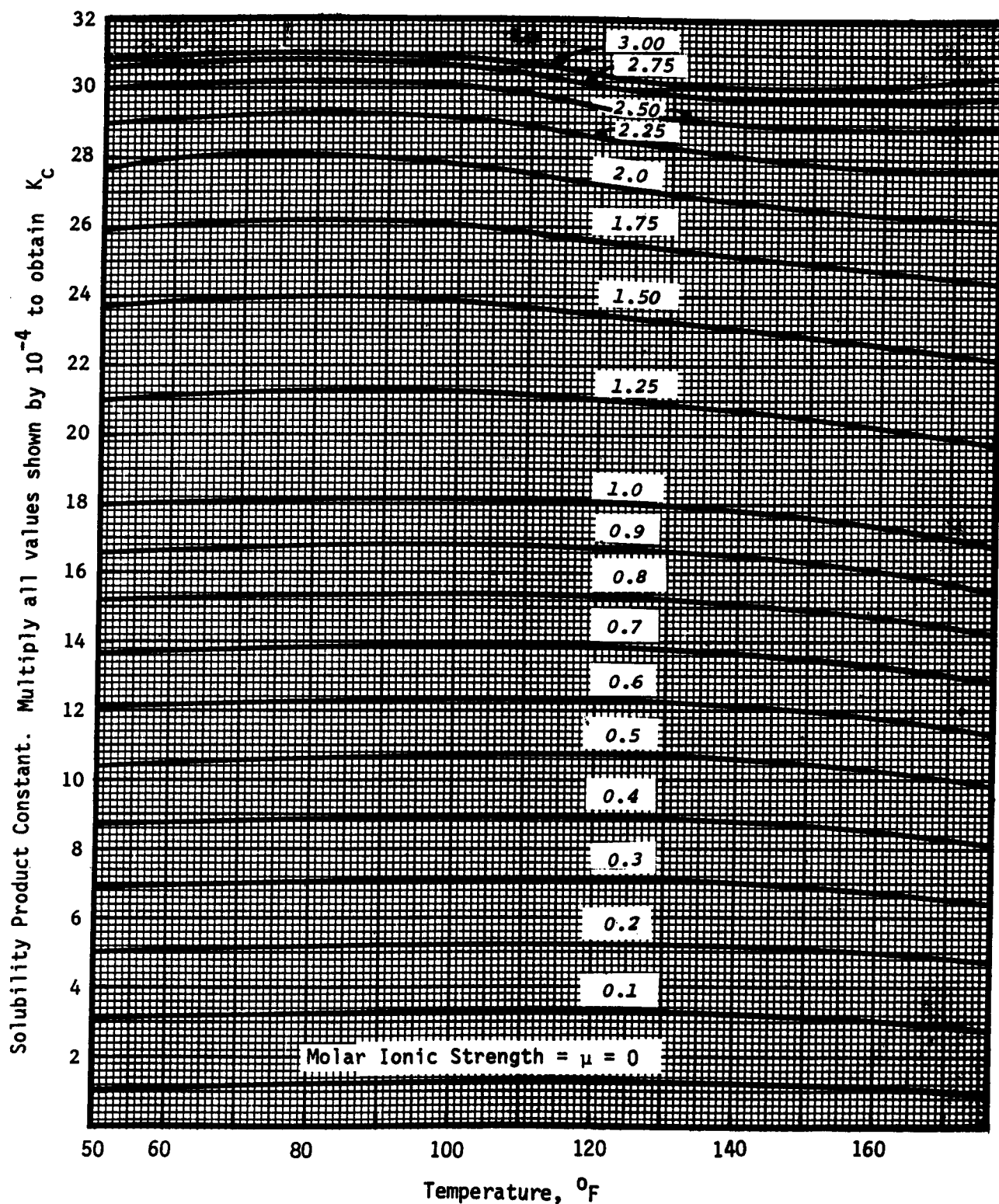
$$S = 1000 \left[((0.146 + 36.8) \times 10^{-4})^{0.5} - 382.9 \times 10^{-5} \right] = 57 \text{ meq/L}$$

Ion	Concentration (mg/L)	Equivalent Weight	Concentration (meq/L)
Ca^{++}	877	20	43.9
$\text{SO}_4^{=}$	1740	48	36.3

Actual CaSO_4 Concentration = 36.3 meq/LS > Actual, so CaSO_4 scale is unlikely.

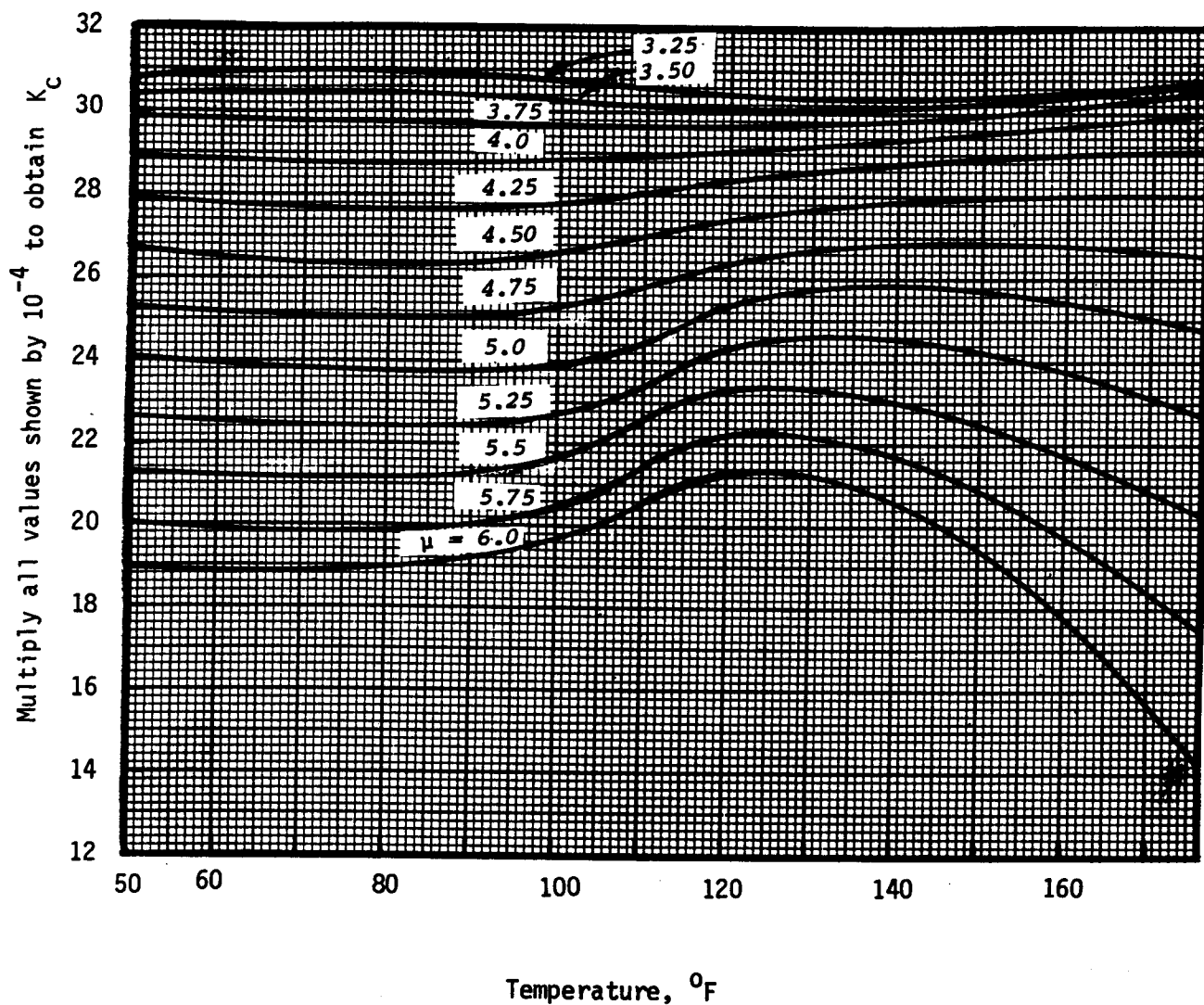
APPENDIX 15

Calcium Sulfate (Gypsum) Conditional Solubility Product Constants

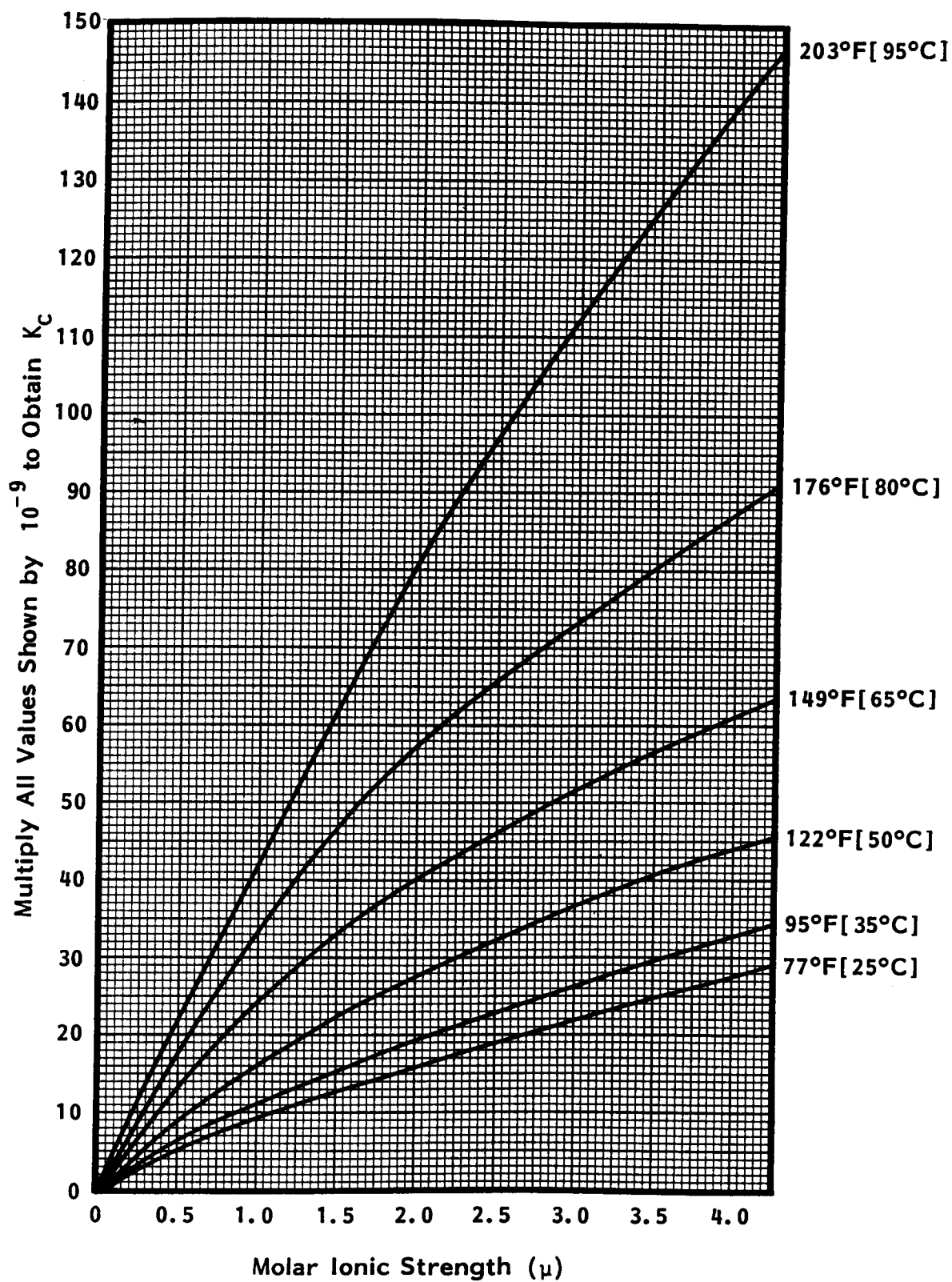


APPENDIX 15

Calcium Sulfate (Gypsum) Conditional Solubility Product Constants (Cont'd.)

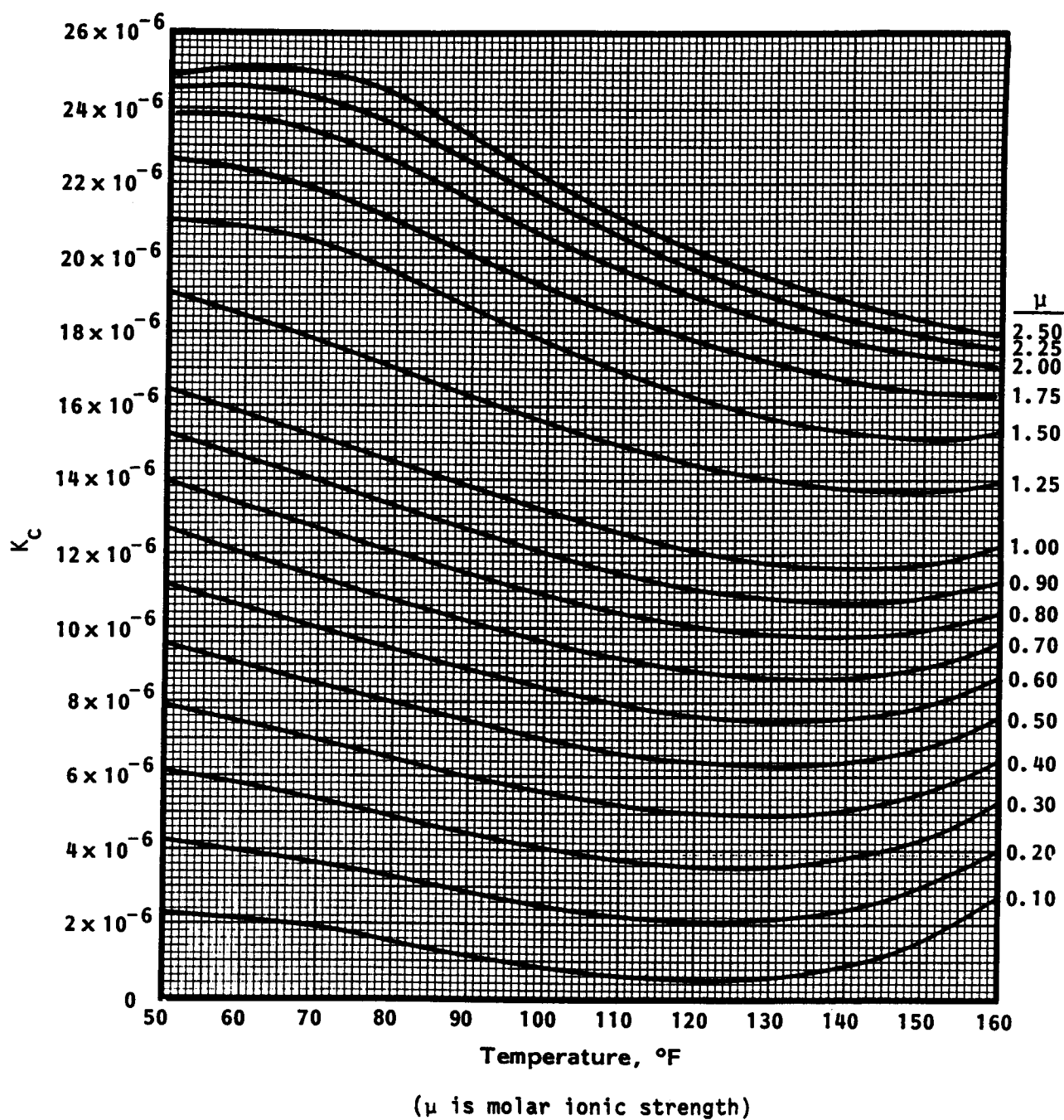


APPENDIX 16
Barium Sulfate Conditional Solubility Product Constants

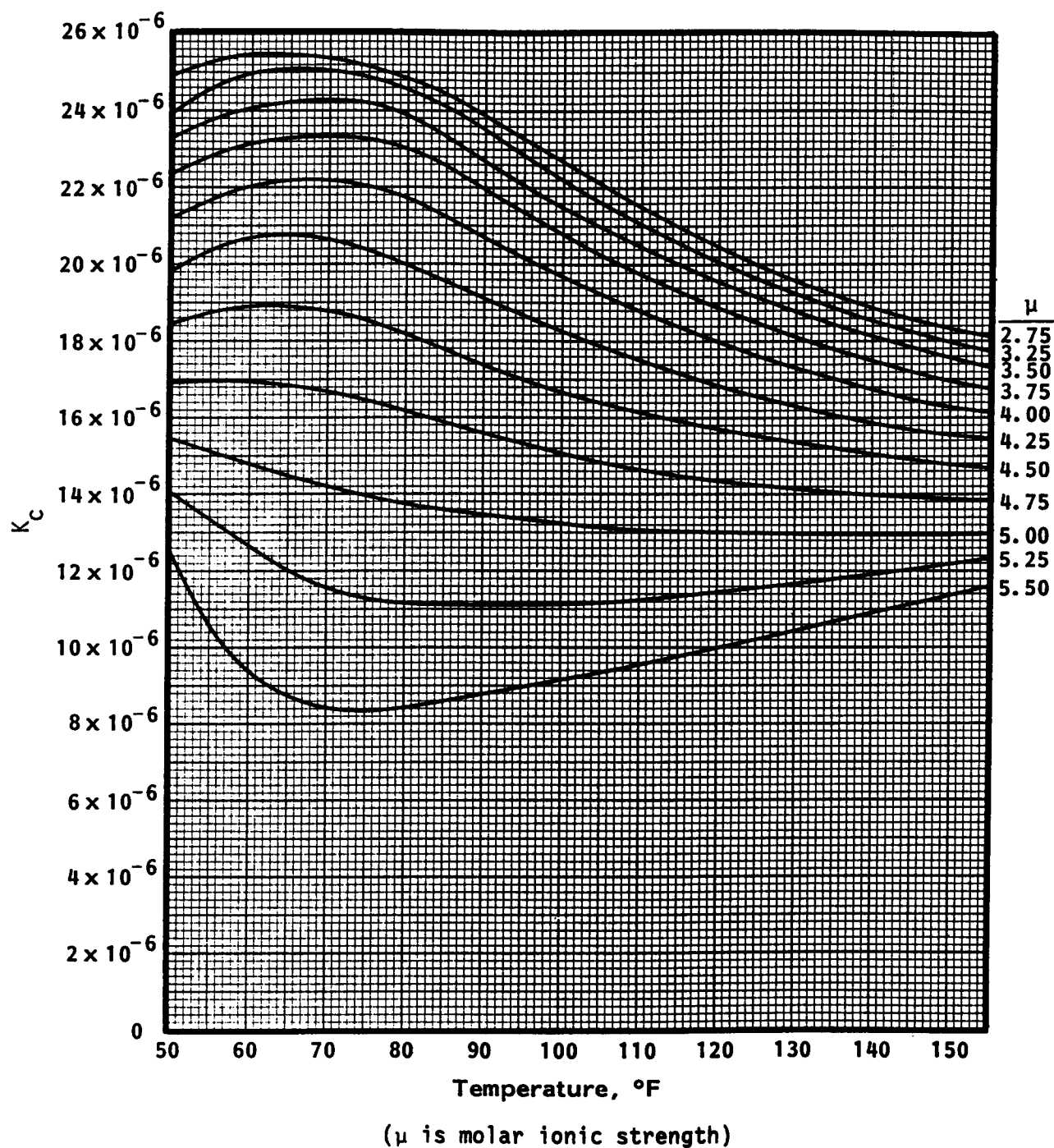


APPENDIX 17

Strontium Sulfate Conditional Solubility Product Constants



APPENDIX 17
Strontium Sulfate Conditional Solubility Product Constants (Cont'd.)



APPENDIX 18**Toxicity of Hydrogen Sulfide Gas**

Concentration	Result
10 ppm	Can be smelled. Safe for 8 hours of exposure.
100 ppm	Kills smell in 3 to 15 minutes. May sting eyes and throat.
200 ppm	Kills smell quickly. Stings eyes and throat.
500 ppm	Loss of sense of reasoning and balance. Respiratory paralysis in 2 to 15 minutes. Prompt artificial resuscitation required.
700 ppm	Unconsciousness within 15 minutes (maximum). Cessation of breathing and death will result without immediate artificial resuscitation.
1000 ppm	Immediate unconsciousness. Permanent brain damage may result unless rescued promptly. May be fatal within 30 minutes.

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